

**EVALUATION OF RISK CAUSED BY WASTEWATER  
DISCHARGES FROM THE PETROCHEMICAL SPECIAL  
ECONOMIC ZONE (PETZONE) TO THE MUSA BAY  
(PERSIAN GULF - IRAN)**

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## ABSTRACT

This study investigated the presence of polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbon (TPH) in the wastewater effluents of PETZONE and sediments of the Musa Bay (around the PETZONE coastal area) from Jun 2009 to Jun 2010.

The primary objectives of this study were to evaluate the sources of pollutants and each pollutant's distribution, concentration and contamination degree, as well as to assess the biological response to these stressors based on the ecological risk. The levels of TPH concentration in the study area were found to be relatively moderate (with an average value of 48.98  $\mu\text{g/g}$ ) compared to the world-wide chronically oil-contaminated locations. Also the average concentration of PAHs was found to be lower than the guideline values (with a mean value of 3.40  $\mu\text{g/g}$ ) in the study area and other parts of the bay. The source analysis based on the isomer pair ratios and also the principle component analysis showed that, in addition to petrogenic input as a major source, pyrolytic inputs are also a source for PAHs. Also, the results of Chronic Potency Ratio of PAHs showed that, all the sampling stations meet the guideline value with the exception of the stations 3-BI and 4 (which are located in the vicinity of the Bandar-e-Imam Khomeini petrochemical company). Furthermore, the contamination factor showed that, the study area can be classified as slightly polluted and be categorized as of low ecological risk. Also, the average value of AMBI was 2.66, so the study area can be categorized as slightly polluted based on this index. Owing to this index, the pollution level of most of the stations varied between undisturbed and moderately polluted (except stations 3-BI and 4).

In the case of environmental impact assessment (EIA), the PETZONE effluent outlets were monitored and showed that, the average concentrations of PAHs were lower than the guideline values at all the stations; thus the effluents of the study area can be considered unpolluted. Also, the average concentration of TPH was lower than the guideline value at all sampling stations with the exception of the effluent outlets of Razi and Bandar-e-Imam Khomeini petrochemical companies which are proximal to Musa Bay and they may have an adverse impact on the aquatic ecosystem of the bay.

The result of the Risk Priority Number (RPN) based on TPH showed that, Bandar-e-Imam Khomeini petrochemical company can be classified in a category of important environmental aspect, and Razi and Shahid Tondgouyan petrochemical companies can be categorized as moderate environmental aspects; while the rest of the petrochemical companies can be classified as low environmental aspects. Thus, Bandar-e-Imam Khomeini petrochemical company should mitigate the risk and it requires executive management attention and control actions, while, Razi and Shahid Tondgouyan petrochemical companies should plan to manage the risk and decrease it during the long term. In addition, the results of RPN based on PAHs demonstrated that, all the sampling stations can be classified as low environmental aspects, thus more control actions is not necessary but they should be monitored during their activity.

**Keywords:** Ecological Risk, Environmental Impact Assessment, RPN, TPH, PAHs, AMBI, PETZONE, Musa Bay.

## ABSTRAK

Kajian ini menyiasat kehadiran hidrokarbon - hidrokarbon aromatik polikitar (PAH) dan hidrokarbon petroleum terjumlah (TPH) dalam efluen air buangan. Dalam penyelidikan ini, pemantauan endapan (di sekitar pesisiran PETZONE) dan efluen air buangan telah dilakukan mulai bulan Jun 2009 sehingga Jun 2010.

Tijuan utama penyelidikan ini adalah untuk menilai punca pelbagai jenis pencemaran dan taburan setiap pencemar, kepekatan dan tahap pencemarannya dan juga untuk mengukur respons biological kepada tekanan tekanan ini. Tahap kepadatan TPH (48.98  $\mu\text{g/g}$ ) dalam kawasan kajian agak sederhana berbanding dengan lokasi diseluruh dunia yang mengalami pencemaran kronik. Konsentrasi PAH (3.40  $\mu\text{g/g}$ ) adalah lebih rendah dari bahagian lain Teluk Musate tapi mendekati nilai garis panduan kualiti mendapan NOAA. Keputusan analisis punca menunjukkan bahawa selain dari punca petrogenik sebagai punca utama, (disebabkan oleh jumlah minyak dan gas dalam Teluk Parsi), pirolisis juga merupakan satu sumber bagi PAH. Keputusan-keputusan Chronic Potency Ratio bagi PAH menunjukkan bahawa ia tidak menepati garis panduan sama sekali di semua stesen-stesen kecuali stesen-stesen 3-BI dan 4 (yang terletak di sekitar syarikat Bandar-e-Imam Khomeini petrokimia). Tambahan pula, sekali faktor, pencemaran menunjukkan Kajian boleh tergolong sebagai sedikit tercemar dan rendah dari segi risiko ekologi. Juga, nilai purata AMBI adalah 2.66, supaya kawasan kajian boleh dikategorikan sebagai sedikit tercemar berdasarkan indeks ini.

Dalam kes Penilaian Impak Alam Sekitar, punca efluen PETZONE telah dipantau dan keputusan menunjukkan bahawa kepadatan purata PAH lebih rendah dari nilai-nilai garis panduan di semua stesen; oleh itu efluen di kawasan kajian dapat dipertimbangkan sebagai bersih. Juga, kepekatan purata TPH adalah lebih rendah dari nilai garis panduan sama sekali kecuali efluen dari syarikat petrokimia Razi and Bandar-e- Imam Khomeini yang letaknya berdekatan teluk Musa.

Keputusan "Risk Priority Number" (RPN) berdasarkan TPH menunjukkan bahawa petrokimia Bandar-e-Imam Khomeini boleh diklasifikasikan dalam kategori aspek alam sekitar tinggi, dan petrokimia Razi and Shahid Tondgouyan dikategorikan dalam kumpulan aspek alam sekitar sederhana; manakala selebihnya petrokimia boleh digolongkan sebagai mempunyai aspek alam sekitar rendah. Keputusan "Risk Priority Number" (RPN) berdasarkan PAH menunjukkan bahawa, semua petrokimia boleh digolongkan sebagai mempunyai aspek alam sekitar rendah.

**Kata kunci:** Risiko ekologi, penilaian impak alam sekitar, RPN, TPH, PAHs, AMBI, PETZONE, Musa Bay.

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## LIST OF ABBREVIATIONS

AMBI	AZTI Marine Biotic Index
ASEAN	Association of Southeast Asian Nation
Acy	Acenaphthylene
Ant	Anthracene
Ace	Acenaphthene
BaA	Benzo(a)anthracene
BbF	Benzo(b)fluoranthene
BkF	Benzo(k)fluoranthene
BaP	Benzo(a)pyrene
BghiP	Benzo(g,h,i)perylene
Chr	Chrysene
CA	Cluster analysis
CF	Contamination Factor
Cd	Contamination Degree
Cm	Centimeter
DbahA	Dibenzo(a,h)anthracene
DOE	Department of Environment
Dw	Dry Weight
ERA	Ecological Risk Assessment
ERA	Environmental Risk Assessment
EIA	Environmental Impact Assessment
EHA	Ecosystem Health Assessment
Flu	Fluoranthene
Flur	Fluorene
FAO	Food and Agriculture Organization
g	gram
GESAMP	Group of Experts on the Scientific Aspects of Marine Environmental Prot
IP	Indeno[1,2,3,(c,d)]pyrene
ISQVs	Interim Sediment Quality Values
kg	Kilogram

Km	Kilometer
l	Liter
m	Meter
mm	Millimeter
mg	Milligram
µg	Microgram
MEQ	Marine Environment Quality
MEH	Marine Ecosystem Health
ND	Below the method detection limit
Na	Naphthalene
PETZONE	Petrochemical Special Economic Zone
Phen	Phenanthrene
Py	Pyrene
ppm	Part per million
ppb	Part per billion
PCA	principal components analysis
PAHs	Polycyclic Aromatic Hydrocarbons
ROPME	Regional Organization for the protection of the Marine Environment
SD	Standard Division
TPH	Total Petroleum Hydrocarbon
TDS	Total dissolved Solid
UNEP	United Nations Environment Program
UNDP	United Nation Develop Program
USEPA	U.S. Environmental Protection Agency
WQI	Water Quality Index

## **CHAPTER I: INTRODUCTION**

In recent decades, developing countries have contaminated their water extensively. The contamination can result in physical and biological modifications as well as chemical contamination due to the toxic and inappropriate elements. This contamination decreases water quality and may make water unusable for most consumption. In 1990, the Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) defined marine pollution as follows (This definition emphasizes on contamination of human origin, not natural contamination):

marine pollution includes the direct or indirect human introduction of any type of materials or energies to the marine environment (including seashores and creeks) that may have an inappropriate effect and endanger on the marine life and human health and also limit marine activities or decrease the quality of marine waters and their desirability (Kennish, 1997; Marcus, 2004).

Chemical materials are one of the most important types of water contaminants and originate from natural resources, mining, industries (such as Petrochemical companies), and other sources of pollution (point and non-point sources of pollution). Petrochemical companies are one of the point source of pollution. Petrochemical industries are those industries in which the hydrocarbons of natural oil and gas are transformed into chemical products (Monavari, 2001; Mostajabi, 2008). The pollution caused by these industries has become a cause for concern, and protecting the environment from the adverse impacts of the petrochemical is a major challenge all over the world. These impacts include not only the biological factors of the ecosystem but also water resource quality and human health (Esmaeli Sari, 2002). Thus, conducting environmental impact assessment (EIA) in such

industrial areas and monitoring the influenced area is very important. One of the areas which can be influenced by these kinds of industries is aquatic environment that is located close to these industries.

The contamination of marine waters has endangered marine life cycle and, consequently, life cycles throughout the planet. Land runoff, industrial waste, navigation and transportation extensively release chemical pollutants into the seawaters such as petrogenics like Polycyclic Aromatic Hydrocarbons (PAH), persistent toxins like heavy metals, nutrient and Total Suspended Solid (TSS); thus, ecological and biological conditions are influenced by these pollutants (Yap, 2005). In the marine environment, organic and inorganic compounds cause serious problems because excess concentrations can alter the characteristics of marine ecosystems resulting from several kinds of hazardous and toxic materials which can bioaccumulate in biological communities. Moreover, studies show that these kinds of compounds have high carcinogenic and mutagenic characteristics. Therefore, determining these types of contaminants (such as hydrocarbons and heavy metals) concentration and their distribution in water and sediment is a key part of the evaluation and assessment programs in coastal areas because they help us to calculate and determine the contamination degree (CD), categorize these pollutants (according to their chemical behavior) and potential threat to the environment and also determination of pollution sources (Neff, 1979; Neff, 2002; Loska & Wiechula, 2003; Morillo, Usero & Rojas, 2008).

Moreover, studies showed that, Bio-assessing and surveillance are applicable methods of monitoring the ecological health status of ambient seawater (receiving water), (Burger & Gochfeld, 2004). Macro benthic organisms are important bi-indicators for

assessing the ecological risk (ERA), health status and impacts of chemical contaminants due to:

- Their vicinity to sediment,
- High sensibility to the chemical compounds of organic,
- Non-organic substances,
- Their ability to up take and accumulate different kinds of compounds.

Benthic organisms are the main connection of the trophic chain in aquatic environment and they can transfer compounds to higher trophic levels. Important factors which have influence on accumulation by benthic organisms are as follows:

Concentration of chemical contaminants, season, size, hydrodynamic parameters of the aquatic environment ( Boyden & Phillips, 1981; Beltman, Clements, Lipton & Cacela, 1999; Caçador et al., 2011; Coccioni, 2000; Mucha, Vasconcelos, & Bordalo, 2005; Foster, Armynot du Châtelet, & Rogerson, 2012;).

Therefore, to prevent further destruction of the marine aquatic environments and revitalize its biological and environmental resources, marine environmental protection and management must be considered as seashores and seas are developed and used. Thus, in addition to reformation and restraining measures following the accurate diagnosis of sources of water pollution, should be prevented by fundamental programming enacted by authorities. Increasing the general awareness of contamination and its undesirable consequences on living organisms and presenting scientific solutions for the problem are



also important and fundamental measures and absolutely essential to keep the marine environment clean and sustainable.

Persian Gulf is one of the most sensitive and unique ecosystem which is located in the ROPME Sea Area (RSA: that is from the end of the Persian Gulf in the West to the north eastern part of the Indian Ocean). It has the highest oil resources and oil transport activities in the world also it is one of the most important “chokepoints” for oil transport in the world (CEDRE, 2007; Farzinger et al., 2011). Several studies showed that the Persian Gulf is one of the oil-polluted marine area in the world (Price, 1998; Al-Awadhi, 1999; Al-Awadhi & Fatimah, 1999; Deppe, 1999; Nadim et al., 2008). Musa Bay is located in the Northwest of the Persian Gulf and according to previous studies and reports of the Iran Department of Environment, it is important for the whole northwestern coast of the Persian Gulf (Deppe, 1999; Nabavy, 1992; Parsamanesh, 1994).

### **1.1. Problem statement**

The severity of human pressures on aquatic ecosystems has led to serious attempts to protect these invaluable resources and he attempt to know about the ecological health status and assess possible ecological effects.

According to the importance of this valuable and unique aquatic ecosystem and the importance of petrochemical complexes as emission sources and point sources of a wide range of chemical substances, the problems addressed in this research are as follows:

1. What are the sources of the petroleum hydrocarbons in the aquatic environment of Musa bay (anthropogenic or/and lithogenic)?

2. Is the effluents of petrochemical special economic zone (PETZONE) contaminated with organic pollutants and is their physical and chemical characteristic complied with the established guidelines?
3. What are main stressors and their effects on biological community structure (due to exposure)?
4. How do biological systems respond to the stressors?

## **1.2.Hypothesis**

High concentrations of chemicals pollutants due to anthropogenic sources, such as navigation and transportation, exploitation (Oil and natural gas resources), seashore development, and drilling are the most important pressures on the ecosystem of the Persian Gulf (Sheppard, Price & Roberts, 1992; Price, 1993).

After the Gulf war in 1991, several researches and investigations were performed on the effects of the Gulf war. In 1996, experiments showed that the coastal area of Imam Khomeini port (in the Musa bay close to PETZONE) was slightly oil-polluted (Massoud, Al-Abdali, Al-Ghadban & Al-Sarawi, 1996; Price, Nature, & Resources, 1994). Thus, after the Gulf war, several studies were performed in the Gulf area by ROPME, Ir. DOE, universities and other governmental and none- governmental organizations.

Therefore , in the present study, due to the vicinity of PETZONE , Bandar-e-Imam Khomeini port and other industries to Musa Bay, the distribution and sources of total petroleum hydrocarbons and polycyclic aromatic hydrocarbons in the sediment of Musa Bay close to the PETZONE (northwest of the Persian Gulf) was monitored. Moreover, the concentration of these factors (TPH and PAHs) in the wastewaters of PETZONE

petrochemical companies was monitored too. Thus there are two hypotheses for each part of research (sediment of the Musa Bay close to the PETZONE coastal area and the wastewaters of PETZONE):

- 1- A- $H_1$ : These pollutants (TPH and PAH) influence the health status of Musa Bay;  
B-  $H_0$ : These pollutants (TPH and PAH) do not influence the health status of Musa Bay.
- 2- A- $H_1$ : The wastewaters of PETZONE petrochemical companies are the main source of oil pollution in this area;  
B-  $H_0$ : The wastewaters of PETZONE petrochemical companies are not the main source of oil pollution in this area.

### **1.3. Background of Study Area**

In the 20th century, several studies showed that the concentration of petroleum compound and heavy metals are increased in marine environments due to the growth of the petroleum industries and the marketing of petroleum products (Patin, 1999). At the first decades of this century, there have been a lot of reports on the changes of marine biological communities due to the crude oil spillage from ship wrecks. After the World War II, scientific researches on the impacts of oil pollution have greatly increased and in 1967 the wreck of the Torrey Canyon in coast of England was used as the first comprehensive study to assess the effects of oil and heavy metal pollution and also their cleanup methods on environmental resources (NOAA, 1991; Baker, 1976). The National Oceanic and Atmospheric Administration (NOAA) and EPA programs have been developed to classify toxicity level of the aquatic sediments by evaluating concentrations of contaminants and

distribution of benthic community as indicators. Moreover, many organizations have provided classifications and guidelines of aquatic sediments including, the Canada Ministry of Environment Ontario Provincial SQGs, the Interim Sediment Quality Values (ISQVs) and Department of Environment Research of New York Sediment Screening Criteria (O'Connor, 1992). Also , many administrative and research institutes were organized to develop and manage marine environment law such as UNEP (United Nations Environment Program) , SIDS (Sudden Infant Death Syndrome), IUCN (International Union for Conservation of Nature and Natural Resources), UNDP (United Nation Develop Program ), FAO(Food and Agriculture Organization), and GEF (Global Environmental Facility).

In addition, the assessment of human impacts on the health of seashore and estuaries biological communities, in different areas of the world has been investigated in several studies (Pearson & Rosenberg, 1978; Gray & Mirza, 1979; Hakanson, 1980; Boesch & Rosenberg, 1981; Warwick, 1986; Chapman, 1989; Ferraro, Swartz, Cole, & Schults, 1991; Wilson & Jeffrey, 1994).

The Gulf's marine environment is becoming progressively important in social, economic, development and strategic objectives of the region (Price et al., 1994). It is located in ROPME Sea Area which comprises the Gulf of Oman and the Persian Gulf with an average area and depth of about 240,000 km<sup>2</sup> and 35 m, respectively (De Mora et al., 2010). The Persian Gulf is characterized by warm and saline water and the depth of the Gulf decreases from east to west with a maximum depth of 90 m in the Strait of Hormuz (Håkanson & Blenckner, 2008) .

Municipal and industrial wastewaters have caused severe problems in different areas of the Persian Gulf, but their effects on ecosystem structure have not been well-recognized.

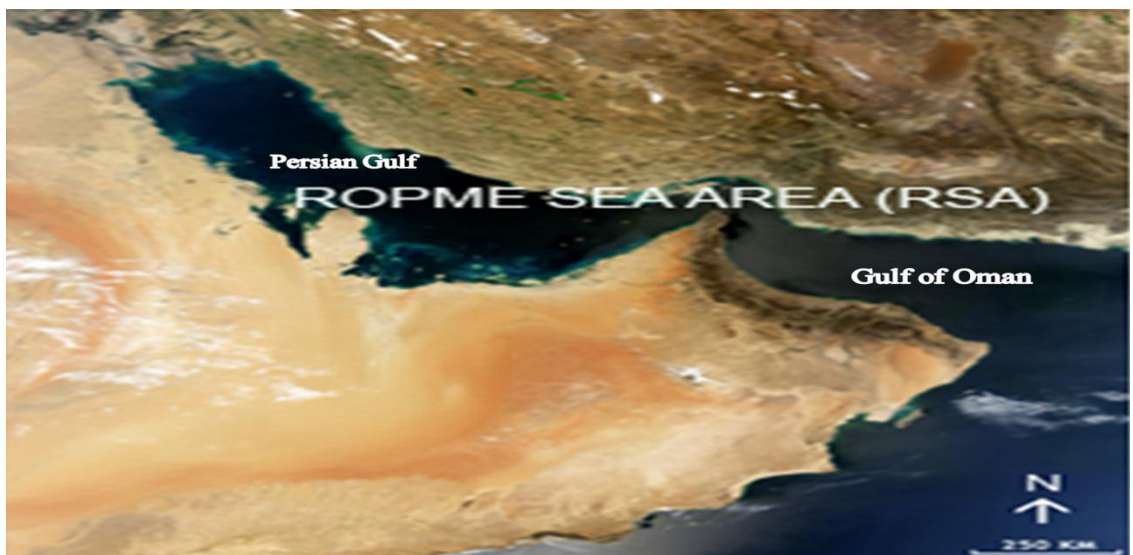
One of the most important ecological problems is the destruction of seashore habitats with high potential and productivity. These have been destroyed as a result of land degradation and sedimentation activities. Sheppard (1992) and Price (1993) have described different types of exploitations, activities and important pressures on the marine and seashore environment of the Persian Gulf. The effects of oil leakage, seashore development and destruction of habitats, all types of wastewater, agricultural compost, drilling and increasing heavy metal contamination in the sediments are the most important pressures on the invaluable ecosystem of the Persian Gulf (Sheppard, Price & Roberts, 1992; Price, 1993).

In the Gulf area, after the Gulf war in 1991, contamination problems and threatening features in the Persian Gulf were given greater recognition, and several studies were conducted to estimate the damage on the Persian Gulf ecosystem, the most significant of which was that by Price et al. (1994). They conducted a broad study with the support of IUCN to investigate the damages resulting from the Gulf war, the widespread leakage of oil and the burning of several well loops. These studies included polluting materials such as oil and heavy metals. Price (1994) concluded that the rate of destruction due to events such as war is greatly dependent on the duration of the stress and the post-stress period such that in one-month or one-year periods, animal communities such as birds will be damaged, while after longer time periods, such as five years or more, living species and communities will be more or less recovered (Price et al., 1994).

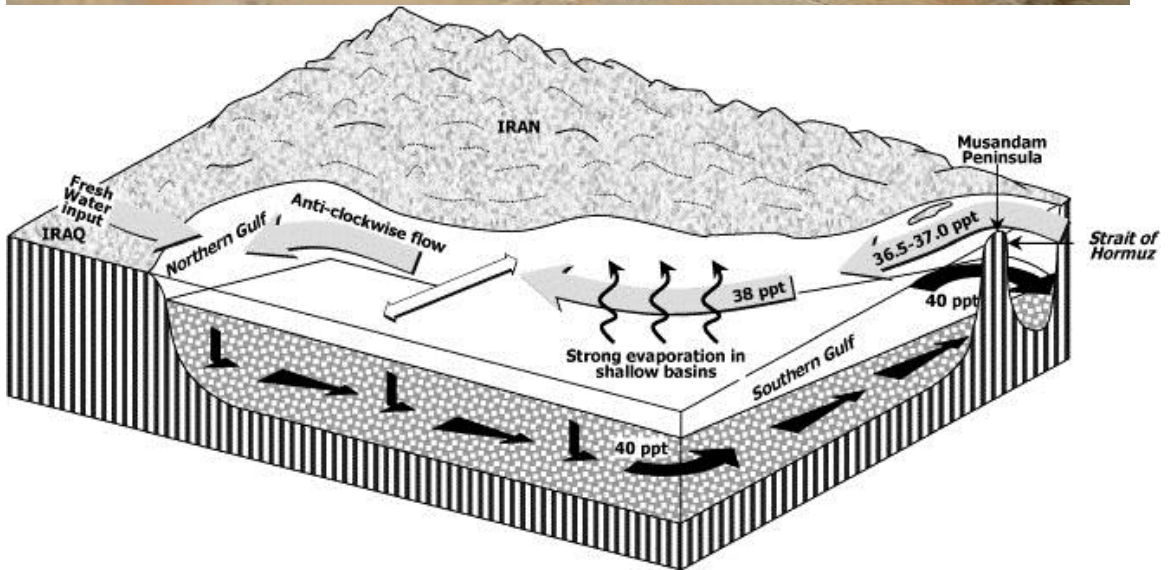
In 1991, immediately after the Gulf war, studies of the population of Ostracoda in waters distant from seashores in the north-western Persian Gulf (Iran side in the 32-54 m water depth) demonstrated that, only two Ostracoda survived from this event and the effects of oil contamination were apparent on their skins (Mostafawi, 2001). Studies of coral-reefs

area, coral fishes and tidal areas in the Gulf declared that, given the biophysical basis and dynamic nature condition, the Gulf ecosystem should recover in 5 years (Downing & Roberts, 1993; Krupp & Jones, 1993; Watt, Woodhouse, & Jones, 1993). Considering the current process of the Persian Gulf (the entrance of shallow waters of the Indian Ocean, the residual currents indicate a surface flow into and a deep flow out of the Gulf through the Strait of Hormuz), the time duration of the complete replacement of the Gulf water has been estimated at 3- 5 years (Brewer & Dyrssen, 1985; Abdelrahman & Ahmad, 1995; Deppe, 1999; Kampf & Sadrinasab, 2005; Pasandeh, 2006). Thus, during this long period, polluting materials will remain in the Persian Gulf for a long period of time (Abuzinada & Krupp, 1994). Therefore, long-term studies are needed to determine the amount of pollutants, their toxicity and stability in the Gulf ecosystem (Price et al., 1994) (Figure1.1).

More than 10000 buoyant vessels pass through this area on a yearly basis, of which more than 75% transport oil and oil products. According to published statistics in 2011, the countries near the Persian Gulf and Gulf of Oman produced 28 % of the world's oil. On a daily basis, 17 million barrels of crude oil are transported via the Strait of Hormuz (Todd, Chessin, & Colman, 1999; Dargin,2007). About 49% of the world's oil production comes from the Gulf states and passes through this old waterway and it holds an estimated about 57-66% of the world oil reserves . Several studies showed that the Persian Gulf is the most oil-polluted marine area in the world, even before the Gulf war and the Gulf oil pollution is about 48 times greater than that of any other similar area on the earth (Al-Awadhi, 1999; Al-Awadhi & Fatimah, 1999; Deppe, 1999; Nadim, Bagtzoglou, & Iranmahboob, 2008; A. Price, 1998).



A.



B.

**Figure1.1.** A.ROPME Sea Area; B. The Gulf Water Current (ROPME 2003)

In the past four to five decades, this area has been the major waterway for oil transport and it has suffered from oil spills into its marine environment thus several studies and Regional Sea Programs, were conducted to estimate the rate of damage to this valuable aquatic ecosystem (Saeed, Al-Muzaini, & Al-Bloushi, 1996;Nadim, et al., 2008;) .

Although several studies (particularly in recent years) have been conducted to assess the different types of pollutants in the Persian Gulf, most of the studies measure different parameters such as oil pollutants and heavy metals and compare the data with the guideline amounts; less has been written on investigating the ecological health status and determining the health level of important and valuable habitats in this area, especially in the northwest of the Persian Gulf.

The most important study about oil pollution of the Gulf was performed in 1996 which was categorised the concentration of total petroleum hydrocarbon (TPH) into four levels as a guideline: Unpolluted area /natural background level (10-15 µg/g), slightly polluted area /upper permissible limits (15-50 µg/g), moderately polluted area (50-200 µg/g), heavily polluted area (> 200 µg/g) ( Massoud, Al-Abdali, Al-Ghadban & Al-Sarawi, 1996).

In 2005, the concentration and distribution of various petroleum hydrocarbons (PHs), chlorinated pesticides and PCBs were determined in biota and coastal sediments in eight countries (Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia and the United Arab Emirates) of the ROPME sea area. The results of this study showed that the extensive marine contamination regarding the organochlorinated compounds and PHs was not observed (De Mora et al., 2010). Also during the last decades the problems of Iran's coastal parts (coastal parts of the Persian Gulf) have increased due to the sectoral



management (Pak & Farajzadeh, 2007). Several internal studies on the chemical pollutants in the Iranian seashores of the Persian Gulf were performed by different organizations. Also, many researches were performed in the northwest of the Persian Gulf especially in Musa bay.

Musa Bay (Khowr-e Musa) is located in the northwest of the Persian Gulf (in Mahshahr City in south west of Iran), which is of importance from the industrial, economic, military and ecological facets. It is a basin with 50 km long connection to the open ocean (longitude of 48 ° and 18 ' to 49 ° and 50 ' E and latitude of and 30 ° and 15' to 30° and 32' N) ; it is not an estuary because there is no freshwater inflow. The tidal range of the Bay is 2 to 3 m and at times can be up to 5 m (in the 89 m deep connection channel) (Deppe, 1999). The tides in the bay are rather semidiurnal. Therefore, broad areas of the surrounding lands are continuously filled and drained.

In general, in this area, the tidal pumping is the main and dominant process which determined the maximum turbidity (Ghaffari, Azizpour, Noranian, Chegini, Tavakoli & Shah-Hosseini, 2011). At the eastern end, water depth of the Bay is between 5 - 18 m while at the western end, it is about 80 m (Tabatabaie & Amiri, 2011). The concentration of suspended sediment is high in the Bay. The bed sediments are composed of mainly silt, however they become coarser in the mouth of the Bay (the width is about 37-40 km) in the Persian Gulf (due to the tidal currents) (Ghaffari et al., 2011; Tabatabaie & Amiri, 2011). It is located in a large cross-border area of intertidal mudflats. A common characteristic of almost all intertidal mudflats is the high productivity which makes them attractive for breeding, nesting, overwintering and migration stop-over grounds for birds and as nursery

ground for many fish species (Deppe, 1999; Pasandeh, 2006; Al-Behbehani & Ebrahim, 2010).

The climate in this area is warm and humid with a maximum temperature of 48 °C (in summer) and the annual rainfall in this region is 196 mm with the westward predominant wind direction ( Namaish, 2009; Godarzi Nik, Shahbazi, & Grigoryan, 2012). The bay has a high salinity usually more than 40 psu which is a little higher than euhaline condition. The concentration of dissolved oxygen (DO) was measured between 3.4 to 8.6 mg/l while, it sometimes decreased to 2 mg/l which is near the critical limits (Doustshenas, Savari, Nabavi, Kochanian, & Sadrinasab, 2009). Musa Bay is a semi-enclosed ecosystem, and several studies have shown that pollution and its adverse effects are stronger in semi-enclosed areas than the open sea. The water circulation in the Persian Gulf is anti-clockwise, and the water exchange rate from the narrow Strait of Hormuz is 3 to 5 years. The water of Musa Bay is exchanged during this time frame. In addition, the semi-diurnal tide naturally dredges and transports sediments and associated pollutants (Deppe, 1999; Kampf & Sadrinasab, 2005; Pasandeh, 2006).

Moreover, several creeks branched out from it, including the Ghazaleh, Majidiyeh, Ahmadi, Jafari, Ghanam, Zangi, Doragh, Bihad, Darvish and Patil creeks (Azymyan, 1987; purokhshoori, 1999; Oveysy & Monshizadeh, 2004; Mooraki, et al., 2008). The numerous tidal creeks of Musa Bay create a unique “land-sea-transition zone” and provide the corresponding life conditions ( Höpner, Ebrahimipour & Maraschi, 2000). The mangrove forests with high biodiversity are another factor of colonization in this unique Bay which can provide a physical habitat and nursery grounds for a variety of aquatic organisms (Ghasemi et al., 2010); for example, Ahmadi creek is one of the claw-

branch of Musa Bay has 106 Ha hand-cultivated forests of a mangrove species, *Avicenna marina* (Sadegh, Behrouzirad, & Amininasab, 2011). Also, in 2000, the Mangrove Afforestation Program was initiated in the coastal area surrounding the aforementioned creeks and Musa Bay, including PETZONE, Bandar-e-Imam Khomeini and the region surrounding Mahshahr oil export terminal to increase the amount of green space around the industrial zones (National Petrochemical Company (NPC), 2006).

Owing to the diverse industries, Musa Bay and Bandar-e-Imam Khomeini has become one of the main economic assets of the north-west coast of the Persian Gulf (Nabavy, 1992; Parsamanesh, 1994). All of the above mentioned points indicate that Musa Bay is very significant and remarkable from the ecological, fishery and biological aspects. However, human activities are enormously effective in this area. Owing to the high water depth in this area, shipping has a special statue in this Bay. Bandar-e- Imam Khomeini is the largest harbor in Iran, which is located in this area and next to the Zangi creek and different products are imported from and exported to this significant harbor (Höpner & Maraschi, 1999). Thus, the Musa Bay channel is the connecting waterway between the seashore waters of Khuzestan province (south of Iran) in the northwest of the Persian Gulf to a broad area with various estuaries that have different depths, which are due to the advancement of sea waters towards land.

According to the different stressing factors, sensitivity and significance of the Khuzestan seashore area for high biological and fishing potentials, there is a serious trend towards identifying such sensitive areas, which is likely to be influenced by assessing the existing conditions and probable dangers that threaten aquatic ecosystems.

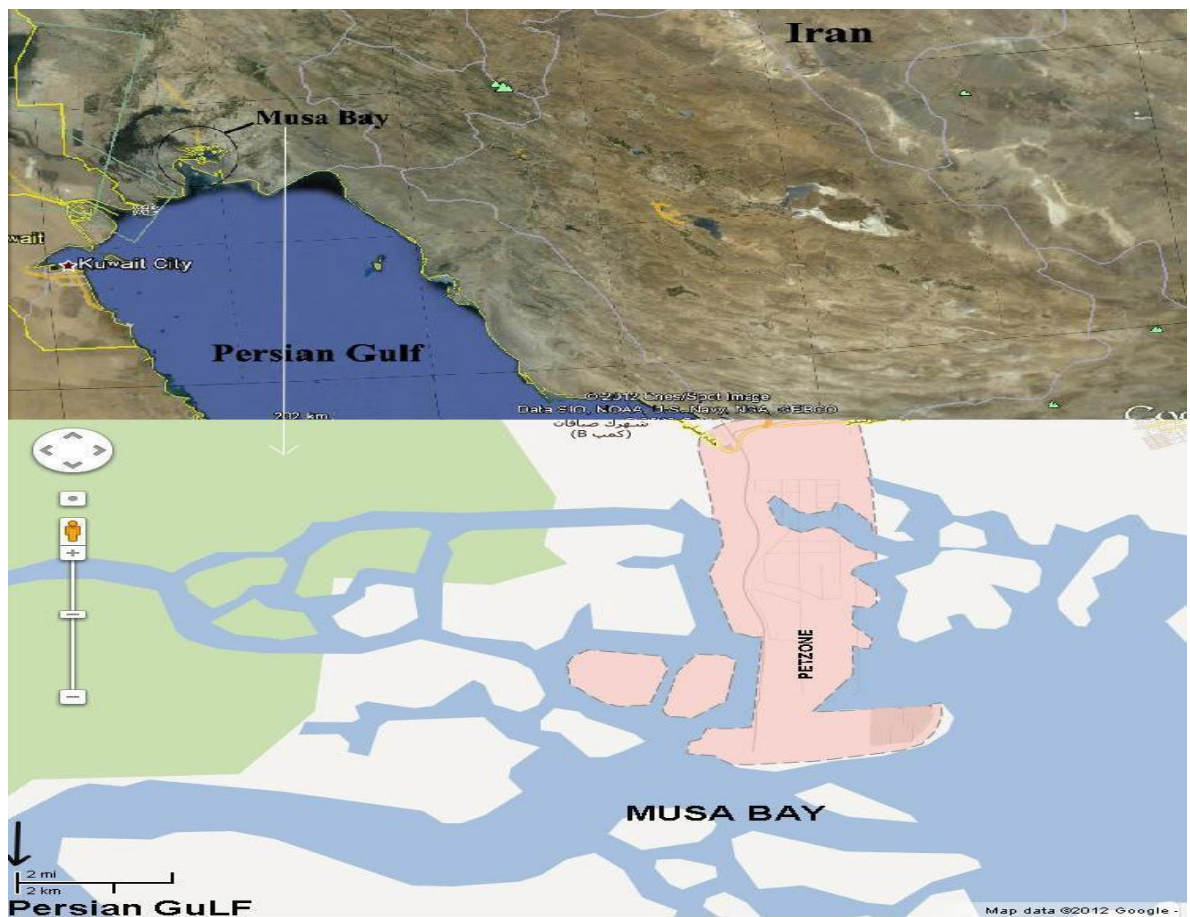
Petrochemical industries have been verified as important emission sources and point source of a wide range of chemical substances, such as volatile compounds, heavy metals and POPs (persistent organic pollutants) (Nadal, Schuhmacher, & Domingo, 2011). One of the most important point sources of pollution in the Musa Bay is Petrochemical Special Economic Zone (PETZONE). In 1993, about 1.22 Km<sup>2</sup> of Musa Bay was drained off for the PETZONE; and in 1997, the Petrochemical Special Economic Zone, with an area of approximately 17 km<sup>2</sup> (about 2600 hectares), was established in south-eastern Iran, at the Persian Gulf shore , within the boundaries of Mahshahr, a district of Bandar-e- Imam Khomeini (BIK). Since the PETZONE was established, some parts of Musa Bay have become enclosed within roadways and construction and, in some areas, divided. (Abdolahpur Monikh, Safahieh, Savari & Doraghi, 2012; Mooraki , Esmaeli Sari, Soltani & Valinassab, 2008). After treatment, the effluents of PETZONE, including the effluents from the Razi and Bandar-e-Imam Khomeini petrochemical companies, are directly discharged into the Bay (Höpner & Maraschi,1999).

PETZONE is composed of 5 sites (the area has recently been developed, and the Bandar-e- Imam Khomeini, Razi and Farabi Petrochemical companies have been added to this area) which are shown in Table 1.1.

**Table 1.1.** Sites and petrochemical companies inside the PETZONE

Site NO.	No. of petrochemical company	Product/s	Application/s	Area Each part (Ha)	Total (Ha)
1	none	none	chemical industries, electrical and electronic, textile, metal and equipment industries, treatment plant, laboratories and QC	240	240
2	4				350
	A-Marun	Heavy polyethylene (HDPE), ethylene, benzene, pyrolysis gasoline, propylene, ethylene glycol.	-	93	
	B- Laleh	Toluene Diisocyanate (TDI), Methyl Di-Phenyl-di- Isocyanate (MDI)	-	12	
	C- Karoon	Toluene Diisocyanate (TDI), Methyl Di-Phenyl-di- Isocyanate (MDI)	-	34	
3	D- Fajr II	none	utility	20	260
	6	-	-	-	
	A-Fan Avaran	methanol, acetic acid, co and hydrogen	-	25	
	B-Shimi baft	MTBE	-	5	
	C-Arvand	PVC (suspension) ,PVC(emulsion), ethylene dichloride(EDC),VCM, caustic soda (100%),sodium hypochloride & chlorine	-	108	
	D-Rejal	in textile, plastics and subordinate petrochemical industries	-	23	
	E-Ghadir	PVC, VCM	-	15.2	
4	F-Shahid Rasooli	acetaldehyde, aldehyde, penta eritritol, sodium formate, depanta)		9	200
	6				
	A-Khuzestan	liquid epoxy resin, polycarbonate epoxy resin, base phenol & phosgene	-	9	
	B-Amir Kabir	ethylene, propylene, 1- butane, benzene, pyrolysis gasoline, butadiene- 1,3 , fule oil , ldpe,lidpe & hdpe.	-	55	
	C-Boo Ali Sina	Aromatic compounds (paraxlylene, orthoxylene, benzene, LPG, heavy aromatic, raffinate, light ENDS, heavy ENDS, C5 cut & SCGO).	-	36	
	D-Shahid Tondgooyan	terfetalic acid, poly ethylene terfetalat	-	15.7	
	ET-Fajr I	-	utility	30	
5	F-Navid Zar	polypropylene		5.7	271
	3				
	A-Banda-e- Imam Khomeini	Ethylene,propylene, butadiene, benzene, toluene & xylenes	-	271	
	B-Razi	Ammonia , urea fertilizer ,diammonium phosphate , sulfuric acid & phosphoric acid.	-	-	100
	c. farabi	Fatlike Andric - DOP- liquid fatlike Andric		-	15

www. petzone.ir



**Fig.1.2.** The location of Musa Bay and PETZONE (Google-Earth6.1.0.5001, 2011)

Thus, because Musa Bay has a limited connection to the Persian Gulf, low capacity for self-purification and high concentration of suspended solids; therefore, the large amount of wastewater discharged into the Bay can be a major water pollution factor, and frequent tides have considerably expanded the scope of the pollution (Malmasi, Jozi, Monavari, & Jafarian, 2010).

According to the importance of this area, several studies were performed to assess the health status of this valuable aquatic ecosystem. For example, Karbassi (1992) conducted a study to determine the concentrations of heavy metals by use of a geochemical index and the natural or standard rate of heavy metal concentrations (in the sediments of the

north western part of the Persian Gulf). In 1996 by the Islamic Republic of Iran by means of the Ghods ship, in which 9 transects in the seashores of Iran (from Musa Bay to Hormuz Island and one station in Abadan which is located in the Khuzestan seashore) were sampled and other samples has been collected in the Booshehr and Bandarabbas provinces (DOE-I.R.Iran,1996). Furthermore, several reports of “ROPME-IAEA” about heavy metal and organic contamination in the ROPME Sea Area (ROPME-IAEA, 1996, 1998, 1999, 2001). In recent decades some researches were performed to determine the concentrations of four elements (zinc, cadmium, nickel and vanadium) in fish and macro benthic communities , surface sediments and waters of the northern part of Persian Gulf, from the strait of Hormuz to Musa Bay (Neff, 2002;Loska & Wiechula, 2003) . The impact of petrochemical special economic zone activities on the health status of Jafari Creek was studied, in 2008 ; the health status of Jafari Creek was investigated by assessing the changes in macro-invertebrate assemblages (Mooraki et al., 2008).

Furthermore, In 2011, the concentration of heavy metals in the sediment and sole fish (*Euryglossa orientalis*) of Musa bay was monitored (Safahieh, Monikh, & Savari, 2011); the variations of heavy metal concentrations in *Liza abu* from the Musa Bay which receives petrochemical wastes, were investigated in 2011 (Safahieh, Monikh, Savari, & Doraghi, 2011); the levels of heavy metals in sediments and Ray Fish (*Dasyatis bennettii*) were studied in Musa Bay and Selech Estuary (Abdolahpur Monikh, Safahieh, Savari, & Doraghi, 2012). In 2012, the concentration of heavy metals (Cd, Co, Cu, Ni, and Pb) was measured the in sediment, benthic, benthopelagic, and pelagic fish species of Musa Bay (Persian Gulf) (Abdolahpur Monikh, et al., 2012).

Moreover, the distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in water from the three creeks of Musa Bay were analyzed, in 2012 (Hosseini, Peery, Karami, Bastami, & Monikh, 2012) based on many other internal reports , studies , thesis and dissertations.

#### **1.4. Objectives of study**

This research started in March 2009 and continued until September 2012 and was sponsored by University Malaya grants (IPPP).

Although the PETZONE environmental office monitors wastewater discharges and the quality of wastewater pathways, there is a lack of information about the oil-polluted wastewater of this petrochemical complex. In the present study, polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPH) in the wastewater of PETZONE and in the sediments of the Musa Bay in the vicinity of the PETZONE coastal area were monitored. The main purpose of this study is to prepare comprehensive database of oil pollution for the PETZONE environmental office and Iran Department of Environment (Ir. DOE).

Though the experts of PETZONE environmental office monitor the quality of the effluents of PETZONE petrochemical companies every day, but there was not enough data about the oil- polluted wastewaters of this petrochemical complex. Thus, this research project would enhance the information on oil-polluted wastewaters of the PETZONE petrochemical industries.

Moreover, the results of research can be applied as managerial tools for the PETZONE environmental office in order to control pollution sources; also the ecological



risk assessment and benthic health status of the Musa Bay will be helpful results to protect living organisms of the Bay. Therefore, it will be of immense value to the Iran Department of Environment (Ir. DOE) and also Regional Organization for the Protection of the Marine Environment (ROPME), in its quest to take corrective measures and take corrective action if needed.

The assessment of the TPH and PAHs status in Musa Bay (in the vicinity of PETZONE) is not an easy task due to:

- The variability in the environmental conditions,
- The non-point sources and point sources of pollution such as Mahshahr oil export terminal, shipping activities and different industries such as PETZONE, also and the vast resources of oil and natural gas,
- The counter-clockwise circulation from the Indian Ocean,
- The deposition of eolian sediments and
- The effects of tidal currents.

Furthermore, there are several limits and difficulty for collecting wastewater samples inside the PETZONE.

Several approaches and methods such as, increasing number of stations inside and outside the PETZONE, temporal assessment, and multiple sediment samplings has been carried out to reduce the impacts.

Several parameters were selected to assess the PETZONE wastewater and sediment quality of the Musa bay. These are the DO (dissolved Oxygen), the COD ( Chemical Oxygen Demanded – in wastewater) , the TPH ( total petroleum hydrocarbon) and the

PAHs polycyclic aromatic hydrocarbons in water/sediment and also the benthic communities are considered as biological indicator.

In summary, the objectives of this study can be arranged as follows:

1. Assess the sediment quality (around the PETZONE) to determine the sources of pollutants (total petroleum hydrocarbon and polycyclic aromatic hydrocarbons) and their distribution, concentration and contamination degree;
2. To measure physical and chemical parameters in the PETZONE effluents (total petroleum hydrocarbon, polycyclic aromatic hydrocarbons, chemical oxygen demand, dissolved oxygen, pH, electrical conductivity , total dissolved solid and temperature);
3. Assess the benthic community based on marine biotic indices because these findings are significant to classify the contamination levels according to biological responds.
4. To determine the ecological risk index and ecological risk assessment (ERA) in Musa Bay;
5. To distinguish environmentally oil impacted sites in the petrochemical special economic zone (PETZONE).

In this dissertation the five-chapter model is used as its framework. The five chapters include:

- Chapter 1: INTRODUCTION
- Chapter 2: LITERATURE REVIEW
- Chapter 3: MATERIAL AND METHODOLOGY

- Chapter 4: RESULTS AND INTERPRETATIONS
- Chapter 5: DISCUSSION , CONCLUSIONS AND RECOMMENDATIONS

## **CHAPTER II: LITERATURE REVIEW**

The literature contains assessment theories of the marine environment according to water and sediment quality and ecological risk assessment (ERA); also assessment and effects of the industrial environment on surrounded aquatic environment based on the impact of wastewater effluents on the quality of receiving waters, environmental impact assessment (EIA) and significant environmental aspect.

### **2.1. Ecological Stresses of Marine Environments**

Although the limited portions of marine environments especially seashore areas , were defined as a marine protected areas (because controlling and protecting the condition of seashores is easier and more feasible) , but these areas cannot be isolated from the effects of different environmental variables, thus the current viewpoint of most marine protection experts is to recognize the main resources of stress and endangers in marine ecosystems and reservoirs and create management plans to decrease or eliminate stress-producing factors (Morillo, Usero & Rojas, 2008).

Marine contamination not only affects the world of fishing industries but may also significantly affect the natural resources which are subjected to overfishing and natural habitat destruction (Lawrence & Hemingway, 2003). Pollutants that affect aquatic ecosystems are categorized into 2 groups: point-source pollutants and non-point-source pollutants. Most of the pollutants that affect marine communities are derived from a variety of chemical pollutants that enter to the aquatic ecosystem via industrial centers and urban discharges, while the rest enter via terrestrial and atmospheric non-point sources. The biotic effects of waste and wastewater are extremely severe in seashore areas.

These effects include the following: eutrophication of delta waters, evolving non-aerobic conditions, poisonous algae blooms, mass-deaths of benthic and epibenthic living organisms and changes in the frequency and variety of fishes and shells of the area. In addition to chemical pollutants, human factors can also be dangerous for seashore areas. The term "Pollution" is referred to a change in the quality of water that destroys biological communities or affects the living and useful features of water, while the term "contamination" refers to the existence of potentially harmful materials at a concentration which does not cause any damage to the environment (Sklivagou, Varnavas, Hatzianestis, & Kanias, 2008).

Traditionally, the point source pollution such as a pipe or ditch was considered as the main point source of water pollution, however, the non-point source pollution has become increasingly destructive due to the development of agriculture production in recent decades and also they are also major causes of water quality problems (Mayio, 1987; Min & Jiao, 2002). Point and nonpoint sources of pollution and their common pollutant categories are shown in Table 2.1.

**Table 2.1.** Point and non-point sources and pollutants

No.	Source		Pollutant categories
1	point source	Municipal wastewater	BOD, Bacteria, Nutrients, Ammonia, Toxics
		Treatment plants	
		Industrial wastewater (facilities)	BOD, Toxics
		Combined sewer overflows	
2	Non- point source	Agricultural runoff	Nutrients, Turbidity, Total dissolved solids, Toxics, Bacteria
		Urban runoff	Turbidity, Bacteria, Nutrients, Total dissolved solids, Toxics
		Construction runoff	Turbidity, Nutrients, Toxics
		Mining runoff	Turbidity, Acids, Toxics, Total dissolved solids
		Septic systems	Bacteria, Nutrients
		Landfills/Spills	Toxics, miscellaneous substances
		Silvicultural runoff	Nutrients, Turbidity, Toxics

(Mayio, 1987)

Thus, since 1990, several studies have focused on assessing and managing the Marine Environment Quality (MEQ) and Marine Ecosystem Health (MEH), including, (NOAA., 1991; Buckley, 1995; IOC, 1996; Percy, Wells, & Evans, 1997; Jamieson et al., 2001; Westhead & Reynoldson, 2004) ; moreover, the assessment of MEH (conditions in the short -term) and MEQ (conditions in the long-term) require monitoring, research approaches, objectives, guidelines and indicators which could be described as follows. ( J ø r g e n s e n e t a l . , 2 0 0 5 ; S u t e r & G l e n n , 2 0 0 8 )

The monitoring process is a main part of assessment and its related data should follow and clarify these objectives;

- To assess the status and trends of marine environmental health;
- How the marine environmental quality is influenced by any types of pollutants;
- To define the interrelationship between different variables;
- To make a distinction between lithogenic and anthropogenic sources;
- To condense information in large-volume data;
- To apply historical and current data as valuable scales to assess temporal trends;
- To provide comprehensive results of monitoring and to provide some recommendations for decisions and policies in the future.

Thus, the main objectives of monitoring assessments have been focused on:

- Estimation of the spatial and temporal distribution of MEQ to choose sampling stations and frequencies;
- To study and estimate the specific effects of each descriptor on pollutant concentration to evaluate pollution effects;

- Estimation of the capability and costs of monitoring operations (Neary, 2009).

It is important to know that the effects of pollution on aquatic life rarely affect a single species of organism, when pollution directly affecting one organism, it indirectly affects other organism (Cooper, 1993). The responses of marine biotic to the introduction of pollutants can be observed at the four level of the biological hierarchy: community, population, organismal and cellular level. The response type is dependent on the type of chemical pollutant, environmental factors (such as temperature, salinity and dissolved oxygen (DO), evolutionary stage and the health status of living organisms while encountering pollutants (Table 2.2).

**Table2.2.** Marine organism responses to chemical contaminants

Biological Level	Biological Response	Effects at the Next Level
<b>Cellular</b>	-Cell Toxication -Metabolic impairment -Cellular damage	Bioavailability of toxic substances <u>Disruption in energetics and cellular processes</u>
<b>Organismal</b>	-Detoxication - Physiological changes -Behavioral changes -Vulnerability to disease -Reduced reproductive efforts -Decreased larval viability - Readjustment in rate functions	-Adaptation  -Altered immunities -Population regulation and adaptation
<b>Population</b>	-Population community changes in age/size structure, biomass , recruitment , mortality, reproduction rate -Ecosystem adaptation	-Negative impacts on species productivity  -Population regulation and adaptation
<b>Community</b>	-Changes in species abundance, distribution and biomass -Altered trophic interactions	-Replacement by more-adaptive species -Reduced secondary production <u>-No change in community structure and function</u>

(Kennish, 1997)

Different types of pollutants include halogenated hydrocarbons such as PCBs (Poly Chlorinated Bi Phenyl), aliphatic or polycyclic hydrocarbons, Organometallic compounds such as methyl mercury compounds and non- organometallic compounds. In addition to

the type of pollutant, the evolutionary stage of living organisms and their health status plays an important role in the existing response (the lower level of the life cycle and the larval stage is the most sensitive life stage to contamination). Moreover environmental factors are also important. Therefore, determining specific contamination effects on living organisms is difficult, particular when the pollution effects are non-fatal (Lawrence & Hemingway, 2003).

Thus, in order to implement aforementioned objectives, it is necessary to focus on many ecological and biological factors and their responses to the introduction of pollutants and also human activities which can affect the marine environmental condition and its quality.

#### **2.1.1. Guidelines and Standards**

The guidelines provide an agreed starting point to set up a site-planning effort (process of reviewing past progress and assessing current and future issues, threats, and needs) as follows:

- Help to organize a complicated process into individual components;
- Minimize the risk of conflict by directly involving representatives of all interest parties and groups;
- Addressing all issues at an initial stage;
- Support for resulting management initiatives by all stakeholders;
- Identify the cumulative effects of adverse impacts to coastal and marine environments;



- Perform an integrated approach by considering all inter-related elements which can affect the site through the collaboration of all interested groups (Gilman, 2002).

Thus, guidelines are able to clarify the trends of physical and chemical variables and also they have high abilities to determine the adverse effects of toxics on human and marine organisms. They arrange limits for the biological, physical, and chemical variables in marine water and sediment (in different activities such as agriculture, industrial, and recreational activities (US.EPA,2001a).

Sediment Quality Guidelines (SQG) have been developed over the last 20 years to assist decision makers in dealing with contaminated sediments (Crane & MacDonald, 2003; Long et al., 1998). List of Sediment Quality Guidelines (SQGs) and Preliminary benchmarks for sediment chemistry and SedQC<sub>SCS</sub> (sediment quality criteria for assessing and managing contaminated sediments at sensitive sites) are shown In Table 2.3 and Table 2.4.

**Table2.3. Sediment Quality Guidelines (SQGs)**

<b>Institution Sediment quality Guideline (SQGs)</b>	<b>Effects ranges</b>	<b>Application</b>
<b>National Ocean and atmospheric Administration (NOAA). ( Long, Smith, &amp; Calder, 1995; Buchman, 2008)</b>	<ER-L: Adverse effects are rarely observed. ≥ ER-L and < ER-M: Adverse effects are occasionally observed. ≥ ER-M: Adverse effects are frequently observed.	Suitable both from fresh and salt water
<b>Canada Ministry of Environmental Ontario Provincial SQGs for Metals and Nutrient. (Persaud, Jaagumagi, &amp; Hayton, 1992) New York Sediment Screening Criteria. ( Long &amp; Morgan, 1990)</b>	<LEL (Lowest Effect level): the effect in the sediment is Considered to be acceptable. ≥LEL and <SEL (Sever Effect Level): contaminated, moderate impact To benthic life. ≥ SEL: contaminated and significant harm to benthic aquatic life.	Suitable freshwater sediment metal guidelines
<b>Hong Kong Special Administrative Region Interim Sediment Quality Values (ISQVs).</b>	ISQVs-Low: adverse biological effects are unlikely. ISQVs-high: sever adverse biological effects are very likely.	Seabed dredged sediment
<b>Development and evaluation of sediment quality guidelines for Florida coastal waters. (Macdonald, Carr, Calder, Long, &amp; Ingersoll, 1996)</b>	TEL (Threshold effect levels): Adverse effects are rarely observed. ≥ TEL and < PEL: Adverse effects are occasionally observed. ≥ PEL (probable effects level): Adverse effects are frequently Observed.	Coastal and marine water
<b>Sediment Quality Criterion (SQC). (Lyman, Glazer, Ong, &amp; Coons, 1987; Pavlou, 1987)</b>	SQC-chronic: Adverse effects are rarely observed. SQC- acute: Adverse effects are frequently observed.	Coastal and marine water

**Table2.4.** Preliminary benchmarks for sediment chemistry and SedQCSCS <sup>1</sup>

Chemicals of Potential Concern (COPCs)	Marine and Estuarine Sediments	Marine and Estuarine Sediments
		SedQCSCS
Polycyclic Aromatic Hydrocarbons (PAHs) (µg/kg DW)		
2-Methylnaphthalene	201	120
Acenaphthene	88.9	55
Acenaphthylene	128	79
Anthracene	245	150
Fluorene	144	89
Naphthalene	391	240
Phenanthrene	544	340
Benz(a)anthracene	693	430
Benzo(a)pyrene	763	470
Chrysene	846	520
Dibenz(a,h)anthracene	135	84
Fluoranthene	1 494	930
Pyrene	1 398	870
Total PAHs	16 770	10 000

1. The SedQC for sites with sensitive habitats were established by multiplying the PEL (CCME 1999; Mac Donald et al, 2003).

DW = dry weight

### 2.1.1.2. Indicators, Methods and Statistical Measures

According to existence of large groups of species in an ecosystem, it is impossible to monitor all organisms, thus it is essential to develop a suite of bio-indicators which can be used to assess health status within that ecosystem (Burger, 2006).

Burger suggested a comprehensive definition of indicator as follows: “Indicator: Index or measurement end point to evaluate health of a system; physical, biological, economic and human” (Kitsiou & Karydis, 2011). Various ecological indices are used to assess the health status of ecosystems. In ecological indices, combinations of different environmental factors are stated as quantitative scales that are primarily useful in environmental management. Thus, tools such as indicators can be used to determine, whether harvesting is fundamentally altering ecosystem structure and function and also it

can be used to suggest management actions which are essential to improve ecological condition within the ecosystem (Carignan & Villard, 2002).

Description of specific Indicators and indices in the marine environment based on water and sediment quality and example of physicochemical and biological indicators are shown in Table 2.5 (Borja et al., 2012; Pinto et al., 2009).

**Table 2.5.**Conventional index for assessment of marine environment base on water / sediment quality (example of physic-chemical and biological indicators)

Method	Index Name	Biological indicators	Physicochemical indicator	Sample timeframe
<b>*Integrate multiparameter</b>	EPA NCA	Chla	Water clarity, DO, DIP, DIN	Summer
	WFD	Chla, Macro-algae, Sea-grass, Macro-benthos	At least 5year data available with monthly sampling in surface layer	
	HEAT	Chla, Primary production Macro-algae, Sea-grass,HAB, Macro- benthos	DO, DIP, DIN,TP,TN, Water clarity	Annual
	IFREME	Chla, Sea - grass,HAB, Macro-benthos	DO, DIP, DIN,TP,TN,SRP Water clarity, sediment organic matter, sediment TN,TP,DIN,DIP	
	Benthic index of Environment	Benthic community	-----	
Benthic Quality Index	Benthic community			
AMBI	Benthic community			
Multivariate AMBI(M-AMBI)	Benthic community			
APBI	Benthic community			
Benthic opportunistic Amphipoda index (BOPA)	Benthic community			
<b>Diversity</b>	Shannon- wiener	Benthic and plankton community		
	Margalaf	Benthic and plankton community		
	K-dominance	Benthic and plankton community		

(Borja et al., 2012; Pinto et al., 2009)

In 2005, Jørgensen et al., classified ecosystem health indices as follows (Jørgensen, et al., 2005):

- First level: based on the presence or absence of specific species;
- Second level: based on the relationships between different types of community or species combinations (such as using the *Nyggard* algae index);
- Third level: based on the concentration of chemical contaminants as an indicator (for example, the concentration of total phosphate in eutrophication);
- Fourth level: based on trophic level (for example, the concentration of chlorophyll *a* (Chl<sub>a</sub>) or the biomass of phytoplankton as an index of eutrophication in lake);
- Fifth level: based on the speed of biological processes as an index (such as primary production to determine aquatic trophic status);
- Sixth level: based on compound indices (such as the ratio between the primary producer and consumers or the production to biomass ratio in an ecosystem);
- Seventh level: based on ecological relationships as an index (biodiversity, size, compatibility and resistance);
- Eighth level: based on thermodynamic variables as an index (such as energy production rate).

The absence or presence of a specific species is one of the common indicators for determining degree of pollution (for example, the Bellan indices: based on characterizing the dominant species as a sign of pollution), but most of the scientists do not recommend to use these indicators due to the natural changes in the density of some indicator species (Warwick & Clarke, 1998).

When indicator species are discussed, the difference between indicator species and bioaccumulative species should be clarified. Bioaccumulative species are mostly used in toxicology studies and are selected based on the type and rate of chemical combination or different toxic species. Indicator species are those species for which presence and frequency are higher than that of other species in the presence of environmental destruction and damage. Such relationships between species presence and pollutants, particularly organic pollutants, have been assessed in various studies. Indicators such as the Bellan indicator (based on the presence of Polychaetes) or the Bellan-Santini indicator (based on the presence of Amphipods) attempt to assess environmental features as a function of the presence of frequent species to diagnose probable pollutants (Bellan-Santini, 1980)

The AMBI index was introduced by Borja et al. (2000), to assess and determine the effects of qualitative sediment conditions on benthic communities (in soft and mud marine sediments). This index is utilized to assess different effects and sources of stress. The advantage of this index is demonstrated by the diagnosis of individual effects in the influenced area. Based on this index, a benthic community is classified according to its sensitivity to increases in stress.

To describe the degree of sensitivity of benthic communities to pollutant overload and environmental stresses, Salen-Picard in 1983 and Hilly in 1984, introduced four ecological groups, followed by the introduction of five ecological groups by Glemarec in 1986. Subsequently, Grall and Glemarec (1997) summarized and classified five groups that are the working basis of the index;

- Group I: Species that are very sensitive to organic enrichment and present under unpolluted conditions such as the specialist carnivores and some of the Deposit-feeders;

- Group II: Species that are indifferent to enrichment (always they found in low densities without significant changes in time) such as suspension feeders;
- Group III: tolerant Species to excess organic matter enrichment but their populations are influenced by organic matter enrichment (Teixeira, Salas, Pardal, & Marques, 2007), such as surface deposit-feeding species;
- Group IV: they are second-order opportunistic species such as small sized polychaetes (subsurface Deposit-feeders) and the last group;
- Group V: they are the first-order opportunistic species. They are deposit- feeders. (Borja, Franco, & Pérez, 2000; Borja, Franco, & Muxika, 2003; Borja, Muxika, & Franco, 2003).

In spite of these criticisms, AMBI index, benthic index, ISD index and Ecological Evaluation Index (EEI) were updated based on the account between the presences of species, stating a kind of pollution. In these indices, due to the responses of benthic organisms to pollutants, they are classified into several ecological groups (Simboura & Zenetos, 2002; Orfanidis, Panayotidis, & Stamatis, 2003; Reizopoulou & Nicolaidou, 2007). Biodiversity indices (such as Shannon-Wiener index, Margalef, Simpson, and K-dominance) have been frequently applied to describe the biological diversity in marine environments. We can quantify and clarify the relationship between diversity of biological organisms and disturbances with these indices (Zaldívar et al., 2008; Kitsiou & Karydis, 2011).

Also, statistical analysis methods are practical for the quantitative monitoring of the marine environment. Two main types of statistical analysis methods that are applied to quantitative assessment of marine environment quality are:

- One-dimensional statistical analysis (it can be classified in several types of methods, Descriptive statistic, Frequency Distribution (FD), Outliers, ANOVA, Correlation and regression),
- Multi-dimensional statistical analysis (it includes Principal Component Analysis (PCA), Cluster Analysis (CA)).

Aforementioned methods have advantages and disadvantages, for example, although Descriptive statistic can provide a statistic summary of central tendency and variability and it can be used to any type of data which define the quality of environment, but a statistic summary cannot provide any final evidence about health status. Frequency distribution (FD) can describe the profile of physicochemical values and forms the basic scale for health status of environment, but normality pre-requisite for probabilistic application is not usually fulfilled. Outliers can Outlying values which are described as the extreme condition of environment, (pollution problem and eutrophic trend) but it has methodology limitations which are due to the non-normally distributed variables. ANOVA can be statistically detected the differences between significant level and compare means of more than two groups or levels but the assumption of normality cannot be met in different variables (fairly often the data are pseudo- replicates or parametric). Correlation and regression can be easily applied to understand the interaction among variables but it required normality (the natural information is distorted by data transformation). The principal component analysis (PCA) can detect the main variables which can have effects on health status or trends but

most of the time it is a preliminary method and cluster analysis (CA) method can be easily applied to classify sampling points based on different variables (Non-parametric), but it has different outcomes (dendrogram) because of several similarity estimations and clustering algorithms (Kitsiou & Karydis, 2011).

## **2.2. Strategies for Monitoring Water Quality**

Assessment of water quality in marine environment should be including a comprehensive monitoring of hydrological, physicochemical, and biological variables (US.EPA, 2001).

Hydrology and hydrodynamic properties such as variation of rainfall and river discharge (stream flow), suspended load, climatic condition, size of water bodies, tidal flow, and circulation; can provide practical and scalable conclusions for water quality monitoring which is related to their direct effect on chemical components and biological communities (US.EPA, 2001). The pattern of physical and chemical features is specific in each coastal water area and most of them depend on geomorphology, climatic, and geochemical conditions in the study area. Thus, it is necessary to determine these characteristics (such as salinity, total dissolved solid, conductivity, redox potential, temperature, and nutrient concentration) (Table 2.6).



**Table 2.6.** General classification of water quality standard in estuary and coastal water

Class	I (Excellent)	II (Good)	III (Satisfactory)	IV (Passable)	V (Poor)
Malaysia					
DO (mg/l)	7	5-7	3-5	3	1
NH3-N	0.1	0.3	0.9	2.7	2.7<
NO2	----	0.4	0.03	5	----
NO3	-----	7	----	----	----
TP	----	0.2	0.1	----	----
TSS	25	50	150	300	300<
TDS	25	50	150	300	300<
PH	5-8	3-5	3	1	-----
EC(umhos/cm)	1000	1000	----	6000	-----
Class	I	II	III	IV	V
Thailand	Natural resource preservation	Coral reef conservation	Aquaculture	Recreation	Industrial, ports and Residential districts area
DO (mg/l)	not less than 4	not less than 6	not less than 4		
NO3 (µg /l)	not exceed than 20	not exceed than 60			
PO4 (µg- /l)	not exceed than15	not exceed than45		not exceed than15	not exceed than45
Unionized Ammonia (µg /l)	not exceed than 70	not exceed than 100		not exceed than 70	
Salinity	any change shall not exceed 10% of the minimum salinity				
Suspended solid	an increase shall not exceed the average value within 1 day, 1 month or 1 year [4] added by its corresponding deviation value				
PH	7-8.5				

(Selangor Water Management Authority, 2005; USEPA, 1991)

Water temperature is one of the main variables influencing the physical, chemical, and biological processes and it is influenced by currents (marine currents), climatic and geographic conditions. The main effect of temperature in aquatic areas is that the temperature has a direct correlation with growth rate of aquatic organisms (US. EPA, 2001).

The other fundamental factor that its concentration is used as operational indicators of pollution in aquatic areas is dissolved oxygen (DO). It largely affects all chemical and biological reactions, and is vital for all types of aquatic life. Several researches showed that

if the percentage of oxygen saturation decreases to 20% ( $\text{DO} < 2 \text{ mg/l}$ ); key species of benthic organisms will die (Håkanson & Blenckner, 2008).

The other important variable for assessment of water quality is pH which can show the acid balance and in most unpolluted marine water it has been recorded between 6.0 and 8.5 (USEPA, 1991). Thus, its balance can be changed by industrial discharge (effluents from different sources and different characteristics). For example, higher values of pH often occur at eutrophic condition, and also salt lake and groundwater discharges.

Next important factors are turbidity and suspended solids which can reflect the water clearness and transparency. Thus there are important indicators describing the optical characteristics of water (Håkanson & Blenckner, 2008).

Salinity is the other factor that can describe the concentration of dissolved salts and ions in aquatic environments which is very important for growth rate and reproduction in aquatic ecosystems. In addition, it can affect the flocculate of suspended particles, which is the operational bio-indicator in estuary and coastal waters (it is the indicator of water clarity) (USEPA, 2001; Håkanson & Blenckner, 2008).

Also, biological communities are widely affected by biogeochemical reactions that also play vital roles in regulating the biogeochemical balances in the aquatic environment. Thus, Bio-monitoring is a useful tool for assessing the quality of the aquatic environment (Ostroumov, 2005). The response of organism and the methods were mentioned in pervious sections.

Other components such as heavy metal and petroleum hydrocarbons are other factors that are analyzed to assess water quality; although, many researchers have indicated

that these parameters cannot logically assess water quality since water bodies, especially estuary and coastal waters, are extremely dynamic and heterogeneous.

### **2.3. Strategies for Monitoring Sediment Quality**

Water quality assessment is not enough to protect aquatic ecosystems and assessment of sediment quality is essential for this purpose and also biological communities are directly or indirectly affected by sediment contaminants, especially through leaching and re-suspension processes, which can increase the bioavailability of contaminants in aquatic ecosystems (Nascimento, 2007).

Coastal sediments may act as a temporary or long-term reservoir of contaminants accompanied by natural origin compounds. Aliphatic and polycyclic aromatic hydrocarbon compounds and also heavy metals and trace elements are omnipresent components of coastal sediments and derive from natural and anthropogenic sources. The natural concentration of chemical compounds is characterized as a base and background for identifying the portion of anthropogenic sources (GIPME., 2003; Lehr & Keeley, 2005; Sklivagou, Varnavas, Hatzianestis & Kanas, 2008).

Sediment quality assessments should be included the following factors (GIPME, 2003; US.EPA, 2004).

- The use of sampling strategies in different spatial and temporal scales;
- Analysis of the physiochemical and biological variables by laboratory testing (for Estimation of toxicity and bioaccumulation);
- Evaluation of ecological indicators such as the structure of benthic communities.

In general, for the comprehensive assessment of sediment quality, the following principals should be followed:

- 1- The concentration and effect of contaminants depend on the condition of water bodies, specific chemical compounds, the natural properties of the sediment, and the native/original biological communities (flora and fauna). These combinations can be different and individual for different areas. Thus, it is essential to consider the combination of biological, physical, and chemical variables to monitor the marine environment.
- 2- For the reliable assessment of sediment quality, hazard identification, exposure evaluation, determination of the biological effects of pollutants, and risk estimation should be included.
- 3- The assessment of sediment quality should be able to make a distinction between a portion of natural and anthropogenic sources of contaminants.

In general , while a general approach is suggested for sediment quality assessments, approaches and studies should be custom designed to suit the site-specific circumstances such as site dynamics, sediment stability, groundwater flows and fluctuating overlying water conditions (Simpson et al., 2005).

Firstly, the analysis of physical characteristics is the main step in assessing sediment quality. The analysis of particle size estimates the frequency of size fraction of mineral particles in sediment, and defined in percentage of sand, silt and clay. Classification of marine sediments can be based upon size or origin. Size classification divides sediment by grain size into gravel (particles >2 mm), sand (2mm > particles > 63µm), silt and clay

(particles < 63  $\mu\text{m}$ ), (Mud is a mixture of silt and clay). Origin classification divides sediment into five major categories:

- Lithogenous/terrigenous: Composed of fragments of pre-existing rock material
- Biogenous: Composed of hard remains of once-living organisms
- Hydrogenous: Formed when dissolved materials come out of solution (precipitate)
- Volcanogenous: particles that are ejected from volcanoes (such as ash)
- Cosmogenous : derived from outer space (Pinet, 2009; USEPA, 2004).

In addition, particle size can have influence on the concentration of chemical and organic compounds and the structure of biological communities. Thus, Fine particles of sediments (such as silt and clay) adsorb organic and inorganic matter more than coarse particles. Therefore, when the dimensions of particles decrease, the ratio between the surface area of particle and mass increases; so, it can lead to enhanced surface exchange of sediments to accumulate hydrophobic and ionic compounds. (GIPME., 2003; Horowitz, 1991; Szava-Kovats, 2008).

In previous researches, the size of particle was frequently used as normalization for standardizing concentrations of chemical compounds in sediment, while nowadays, Granulometric normalization method does not considered for normalizing chemical compounds. Because ,this method alone is not able to estimate the precise concentration of contaminates due to the extensive grain size separation (Covelli & Fontolan, 1997; Frenz et al., 2003; Horowitz, 1991; Kersten & Smedes, 2002; LINE, 2007; Ravichandran, Baskaran, Santschi, & Bianchi, 1995).

Acidity is the other main physical parameter that directly affects the chemical reaction of contaminants. In acidic conditions, bioavailability of sediment-associated contaminants can be increased and caused an increase in the rate of bioaccumulation (Line, 2007).

### **2.3.1. Chemical Assessment of Sediments**

Chemical analyses may provide information about specific levels of contaminants that if their bioavailability leads to toxicity and bioaccumulation (US.EPA, 2004).

#### **2.3.1.1. Petroleum Hydrocarbons**

Petroleum hydrocarbons are a large group of varied compounds and it may contain several hundreds of individual substances which are varied according to the original source of oil, distillation fraction, and type of emission and weathering of the mixture in the environment. Most of the compounds are made entirely from hydrogen and carbon and the compounds can be classified by number of carbon molecules and arrangement. More carbons in a compound means that, it is less volatile or it has a higher boiling point (Todd, Chessin & Colman, 1999).

Petroleum contamination is a major hazardous compound that causes the greatest concern for aquatic life in marine sediments, particularly in areas close to anthropogenic sources (Baumard, Budzinski, & Garrigues, 1998; Beyer, Jonsson, Porte, Krahn, & Ariese, 2010; Khairy, Kolb, Mostafa, El-Fiky, & Bahadir, 2009; Neff, 2002)

Petroleum hydrocarbons are very dangerous for aquatic life and humans because of their toxicity and accumulation abilities which are dependent upon: hydrocarbon

composition, fraction properties, sources, and natural processes (Neff, 2002; Pauzi Zakaria, Okuda, & Takada, 2001).

Among the Organic pollution of aquatic environments, aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) have received much attention due to their omnipresent distribution in marine sediments. Total petroleum hydrocarbons (TPH) are a broad family of several hundred chemical compounds that are originally derived from crude oil, and polycyclic aromatic hydrocarbons (PAHs) contain two or more fused aromatic benzene rings (Massoud, et al., 1996; Mirsadeghi, Zakaria, Yap, & Shahbazi, 2011; TPH, 1999).

Many studies showed that the concentration of PAH in sediment is an appropriate index of the status of contaminates in marine environments; according to the lipophilic characteristics of polycyclic aromatic hydrocarbons (PAHs), their tendency to accumulate in sediments, their low degradation rate and high stability and also their potential to manifest the eco-toxicological activity (Agarwal, Khillare, & Shridhar, 2006; Fragoso, Hodson, & Zambon, 2006; Guzzella & De Paolis, 1994; Kennish, 1997). Furthermore, the volatile compounds are lost from the water column of effluents (especially refinery wastes) through weathering, and their fate depend on the conditions and hydrodynamics of the receiving water (Wake, 2005).

The approach of sediment clean-up determines the specific method to classify hydrocarbon compounds into different classes and groups based on the limited criteria of the number of carbons with the same properties in physicochemical and toxicities. This classification is called fraction, and provides an accurate and reliable assessment of petroleum hydrocarbon in comparison to previous methods. There is a common rule that

increasing the number of carbons (molecular weight), decreases the solubility of hydrocarbons, and increases their toxicity in aquatic areas (Table 2.7) (MADEP, 2007).

**Table 2.7.** Comparison of Different Hydrocarbon Fractions to Characterize Risk

Aliphatic Hydrocarbons		Aromatic Hydrocarbon	
Recommended	Current MADEP	Recommended	Current MADEP
Fractions	Fractions	Fractions	Fractions
C5-C8	C5-C8	C6-C8 (Benzene, Toluene, Ethylbenzene, Xylene) <sup>a</sup>	---
C9-C12	C9-C18	C9-C12	C9-C10
C13-C18		C13-C15	C11-C22
C19-C36	---	C16-C24	---

In the polycyclic aromatic fraction, the classification of C6-C8 contains BETEX compound (Benzene, Toluene, Ethyl benzene, Xylene) are completely mobile with high volatility, and cannot contribute to accumulation and toxicity in aquatic areas. While, the C9-C12 and C13-C15 fractions are sufficiently soluble in aquatic ecosystems, thus they can be toxic when present in excess and can be accumulated in marine organisms. Very high molecular weight of polycyclic aromatic hydrocarbons is the fraction of C16-C24 which is composed of four or five fused rings of PAH and has low mobility and solubility in aquatic areas (Di Toro, McGrath, & Stubblefield, 2007; MADEP, 2007).

Sources of PAHs in the environment are natural and anthropogenic. One of the main anthropogenic sources of PAHs is industrial wastewater discharges, and their effects can be severely aggravated by the aquatic environment (Jiang et al., 2007; Yunker et al., 2002).



**Table 2.8.** General polycyclic aromatic hydrocarbons properties

PAHs	PAH Water Solubility (mg/L)	Sorption Coefficient (soil log K <sub>oc</sub> )	Partition Coefficient (log K <sub>ow</sub> )	Vapour Pressure (kPa at 25°C)	Henry Law Constant (kPa at 25°C)
<b>Anthracene</b> <sup>1</sup>	0.076	4.15	4.45	2.3 x 10 <sup>-6</sup>	100
<b>Benzo(a)anthracene</b> <sup>2</sup>	0.01	5.30	5.61	2.9 x 10 <sup>-9</sup>	5.6
<b>Benzo(a)pyrene</b> <sup>2</sup>	0.0023	6.74	6.06	7.5 x 10 <sup>-10</sup>	2.8
<b>Chrysene</b> <sup>2</sup>	0.028	5.30	5.16	8.9 x 10 <sup>-8</sup>	5.9
<b>Fluoranthene</b> <sup>2</sup>	0.26	4.58	4.90	6.7 x 10 <sup>-7</sup>	37
<b>Fluorene</b> <sup>1</sup>	1.98	3.86	4.18	4.3 x 10 <sup>-5</sup>	563
<b>Pyrene</b> <sup>2</sup>	0.077	4.58	4.88	3.3 x 10 <sup>-7</sup>	64

1: Low molecular weight PAH

2: High molecular weight PAH

Owing to several studies and scientific researches the concentration of the following PAHs in water and sediment should be monitored:

six low molecular weight, two and three rings aromatics, Naphthalene (Na), Acenaphthylene (Acpy) , Acenaphthene (Acp), Fluorene (Flur), Phenanthrene (Phen), Anthracene (Ant), and 10 high molecular weight, four, five and six aromatic rings, Fluoranthene (Flu) , Pyrene (Py), Chrysene (Chr), Benzo(a)anthracene (BaA) , Benzo(b)fluoranthene (BbF), Benzo(k) fluoranthene (BkF) , Benzo (a) pyrene (BaP), Dibenzo(a,h)anthracene (DbahA) , Benzo (g,h,i) perylene (BghiP) , Indeno (1,2,3-cd) pyrene (IP) (Herzfelder & Golledge, 2004; Lerda, 2009; Semlali, Chafik, Talbi, & Budzinski; Viguri, Verde, & Irabien, 2002).

In addition, several studies have classified the sources of PAHs into two categories, pyrolytic and petrogenic (Li, Xia, Yang, Wang, & Voulvoulis, 2006). Pyrolytic PAHs are formed as a consequence of incomplete combustion although petrogenic PAHs are mainly derived from crude oil and its refined products. Also, pyrogenic and petrogenic sources are typically distinguished based on the ratios of individual PAHs, which are identified based

on molecular mass. Some high-molecular-weight PAHs such as BaA, Chy, BbF, BkF , BaP, IP and DibA are known as toxic PAHs because of their mutagenic and carcinogenic effects on humans and other organisms (Hale et al., 2012; Khairy et al., 2009).

The use of ratios of PAH components of the same molecular weight is well founded as an index to interpret PAH composition and its possible sources, for example molecular indices such as fluoranthene/pyrene are used to identify emission sources and other isomer ratios such as An/ An+Phe and Flu/Flu + Py. Also the ratio of LMW (low-molecular-weight: 2-3 rings PAHs) to HMW (high-molecular-weight : 4-6 rings PAHs) are used to identify the possible emission sources (Li, et al., 2006; Yunker, et al., 2002 ;Semplali et al., 2012 ;Wang et al., 2011; ).

#### **2.3.1.2. Natural Process of Petroleum Hydrocarbon in the Environment**

In general, the solubility of petroleum hydrocarbon in the aquatic environment is widely varied and based on several parameters such as salinity, temperature, pressure, TPH molecular weight, and distribution. The two main processes that cause depletion of hydrocarbons in marine sediment by water are dissolution and dispersion, which is percolated into oily sediment and biological degradation. As a matter of fact, the dissolution process of hydrocarbons directly depends upon the rate of solubility in the two phases (oil and water phases) (MADEP, 2007).

##### **2.3.1.2.1. Salinity**

In marine aquatic ecosystems, solubility and bioavailability of petroleum hydrocarbon especially PAHs, are directly controlled by salinity (Schlautman, Yim, Carraway, Lee, & Herbert, 2004). For example, the solubility of TPH in fresh water can be

two times more than marine water (Neff, 2002), thus the potential risks of TPH toxicity for marine organisms is increased in areas with low salinity, such as estuaries and coastal zones (Shukla, Gopalani, Ramteke, & Wate, 2007).

#### **2.3.1.2.2. Temperature**

Temperature is one of the main variables in marine aquatic ecosystems. Increasing the water temperature can lead to an increased rate of chemical reactions and metabolic decomposition, and low temperatures can cause decreased rates of dissolved gases (US.EPA, 2001). It can increase the petroleum hydrocarbon solubility, bioavailability, and biodegradation in aquatic areas, thus it causes an increase in the accumulation rate of petroleum hydrocarbon (Feitkenhauer & Märkl, 2003; May, Wasik, & Freeman, 1978; Viamajala, Peyton, Richards, & Petersen, 2007).

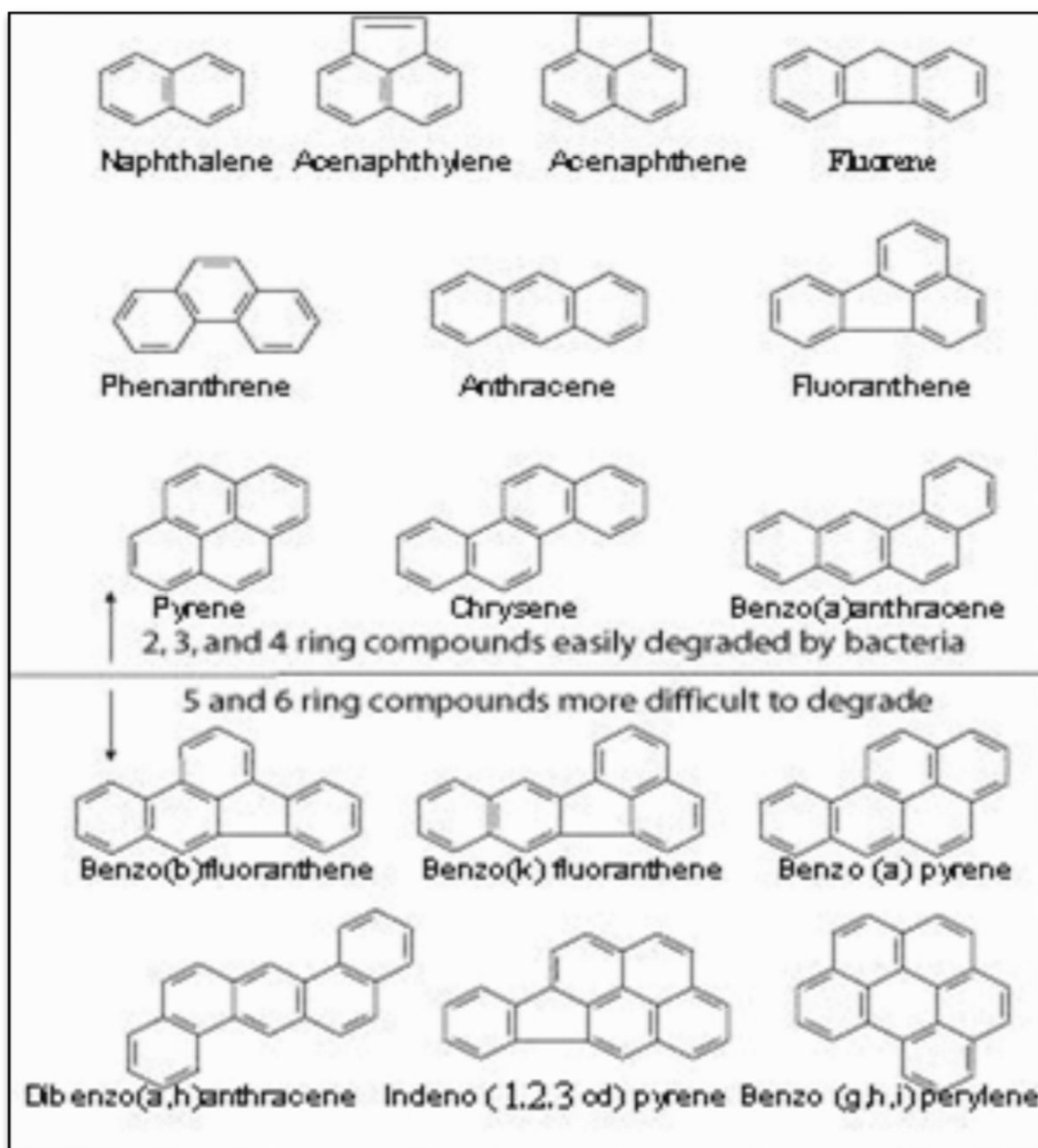
#### **2.3.1.2.3. Solubility and the Molecular Weight**

The solubility of petroleum hydrocarbons decreases when molecular weight and aromatic rings increase. Several studies have showed such a relationship. For example, high molecular weights of PAHs have a greater tendency to leave the water phase and connect with the solid phase (Borja, et al., 2000; Neff, 1979; Varanasi, 1989), also solubility is much higher in PAH angular structures isomers than that the linear isomers. For instance, Phenanthrene has an angular shape and its solubility is 25 times greater than that of Anthracene (with linear shape). Also, the solubility is directly increased when the length of hydrocarbons is decreased (Whitehouse, 1985).

#### **2.3.1.2.4. Petroleum Hydrocarbons Biodegradation**

The PAH fate is categorized in three important topics, PAH release, biodegradation, and bioaccumulation. The PAH components can be degraded via photo-oxidation or microbial biodegradation. Although Schaffner et al. reported that macrobenthos bioturbation notably increased the release of Benzo [a] Pyrene from sediment to water column in Laboratory experiments and also Christensen et al. confirmed the effects of bioturbation on PAH release , Nogaro et al. (2007) reported that PAH release was not significantly influenced by bioturbation ( Nogaro et al., 2007; Qin, Sun, Wang, Yu, & Sun, 2010). Bioturbation is the act of mixing surface sediments as a result of the activity of macrofauna (largely deposit feeders) (Boudreau, 1998). Bioturbation usually can increase the bacterial activity and abundance in sediments, significantly,thus it can increase the biodegradation of PAH. In addition due to the closeness of benthic community to the bottom sediments, they usually ingest large amount of bulk sediments and they are exposed to adsorb PAHs, through their intestines and surface body (Qin, et al., 2010).

The degradation rates of low-molecular-weight (LMW) PAHS such as naphthalene, anthracene and fluorene are greater than those of high-molecular-weight (HMW) PAHs such as benzo(a)pyrene, pyrene and fluoranthene. Based on their physical properties (Table2.8, p.42), the majority of PAH components are high-molecular-weight PAHs and pose minimal risk of mobilization and transport through the environment, whereas low-molecular-weight PAHs are more easily transported through the environment (ATSDR, 1995). Linear alkanes with low molecular weights have a greater degradation rate in comparison to branched alkanes and other petroleum hydrocarbons with higher molecular weights (MADEP, 2007).



**Fig.2.1.** Sixteen PAHs regulated by the EPA (US.EPA)

As it shown in Fig.2.1, the two, three and four ring compounds of polycyclic aromatic hydrocarbons are easily degraded by bacteria however; degradation in the five and six ring compounds is more difficult. The first aforementioned group are as follows: Naphthalene (Na), Acenaphthylene (Acpy) , Acenaphthene(Acp), Fluorene (Flur),

Phenanthrene (Phen), Anthracene (Ant), Fluoranthene (Flu) , Pyrene (Py), Chrysene (Chr), Benzo(a)anthracene (BaA); and the five and six ring compounds are , Benzo(b)fluoranthene(BbF), Benzo(k) fluoranthene (BkF) , Benzo (a) pyrene (BaP), Dibenzo(a,h)anthracene (DbahA) , Indeno (1,2,3-cd) pyrene (IP), Benzo (g,h,i) perylene (BghiP), respectively (Lerda, 2009).

### **2.3.2. Biological Assessment**

Benthic communities directly or indirectly reflect the effect of environmental stressors due to following reasons; their low mobility , their presence/absence are not influenced by diurnal cycles or tidal flux, their classification is based on their sensitivity and resistance to contaminants and hypoxia conditions and existence of predictable patterns of responses for benthic species to variations in marine quality (Borja, Franco and Muxika, 2003; Malloy, Wade, Janicki, Grabe, & Nijbroek, 2007; Pearson & Rosenberg, 1978a; Roesijadi & Robinson, 1994; Tarique, 2008).

Some species (bivalves) are able to bioaccumulate contaminants in their soft tissues, thus it is easier to estimate the concentration of contaminants in their tissues than in marine water column (Tarique, 2008); they have an important ecological role in recycling nutrients between sediment and water and their main food source of commercial fish (Boesch & Rosenberg, 1981; Cesar et al., 2006; Malloy, et al., 2007; Pearson & Rosenberg, 1978).

Gray et al., believe that benthic communities are undoubtedly the best index for diagnosing the health of an aquatic environment. They classified the reasons that benthic communities are appropriate for studying the effects of pollutants as follows:

- Due to the density, any types of materials will eventually be interred in the bottom sediments, and even the pollutants that have been transported in fresh waters to the depth of seashore waters are settled;
- Each organism will die and be ultimately conveyed to materials in the food cycle that are used by benthic organisms. contaminants are associated with organic particles, and therefore, the benthic organisms are severely exposed to pollutants through their food and habitat;
- Benthic organisms have a relatively long life span and are sessile and would thus be exposed to pollutant factors for a longer period of time;
- Benthic invertebrates are sensitive to pollutants;
- Bioturbation activities affect the replacement and interring of xenobiotics in sediments.

Thus, sediments are the historical cemetery of the ecosystem; as they contain a record of previous events and regard as the memory of ecosystem (Gray & Mirza, 1979; Gray, Wu, & Or, 2002).

Generally some benthic species are more resistant than other species to stressors (such as lack DO and a high concentration of toxic materials). As the degree of stress increases, some species can continue to survive, while other species decrease severely or are completely eliminated; in critical conditions, the sediments will become azoic .(Long, MacDonald, Smith and Calder, 1995). Gray categorizes these strategies as belonging to three groups:

- R-Selected Species, which have short life spans, rapid growth, faster time to maturity and resulting in several generations per season;

- K-Selected Species, which have longer life spans, slower growth and higher biomass and produce larger offspring;

- T-Stress-Tolerant Species, which are indifferent to environmental fluctuations and chaos (Gray, et al., 2002).

Previous studies showed that the biomass, abundance, and diversity of benthic communities vary in predictable patterns in response to organic compounds. They reported that the abundance of benthic communities increases along decreased gradients of organic materials (Pearson & Rosenberg, 1978a; Rhoads, McCall, & Yingst, 1978)

In general, Borja provided the comprehensive list of the benthic community based on their tolerance and sensitivity, which is so practical to estimate different indexes such as AMBI and BI (Borja, et al., 2000).

Thus, many research studies have been done to establish standard methods to conduct toxicity tests on sediment, sample collection, storage, and estimation of physicochemical and biological characteristics (Macdonald, et al., 1996; US.EPA, 2000). In recent years, sediment quality has been assessed on the basis of several measurements such as, concentration level of contaminants in sediments, evaluating benthic communities, toxicity tests on specific biological communities, and biomarker assessment.

Toxicity tests of sediments are commonly based on bioassays that determine contaminates toxicity effect on the organism's survival strategy. In this test, specific organisms such as amphipods are selected due to the special characteristics such as sensitivity, abundance, adaptability to salinity and etc. (Cesar, et al., 2006; Green, Chandler, & Piegorsch, 1996; Nipper, Greenstein, & Bay, 1989; Swartz, Ditsworth,



Schults, & Lamberson, 1986). Several indices are frequently applied to study benthic communities but the biomarker approach is a new method for assessing biological responses to the effects of contaminants on different level of biological hierarchy; also it is a useful method for detecting the adverse effects of contaminants on living organisms (specially related to PAH) (Martins et al., 2005; Nascimento, Leite, Sansone, Pereira, & Smith, 1998).

However, most of the researches have concentrated on integration methods which are so useful and practical. This method links chemical analysis with biological effects to understand the responses of benthic organisms to sediment degradation (Anderson, Hunt, Hester, & Phillips, 1996; Anderson et al., 2001; Burton Jr & Scott, 1992; Carr et al., 1996).

#### **2.4. Ecological Risk Assessment**

As defined by the Environmental Protection Agency (EPA), ecological assessment is a process that investigates the harmful and inappropriate or adverse ecological effects that result from the exposure of an environment to one or more stresses(US.EPA, 1992). According to this definition, potential risks at different biological levels, from the individual to the community and ecosystem, can be investigated. The quality of marine environments is normally monitored by various parameters of water, sediment and aquatic organisms.

An ERA (ecological risk assessment) process includes planning, data analysis, results, hypothesis presentation and the investigation of possible risks and severe ecological effects; thus, the framework of ERA consists of three phases as follows: problem

formulation, analysis (characterization of exposure and characterization of effects), and risk characterization (US.EPA, 1992a).

Biological monitoring is mainly conducted by determining the presence or absence of bioindicators and is not a direct estimate of biological effects of contaminants; because the observed changes may be due to other stresses (natural or anthropogenic) in addition to the contamination. If the stress is chemical stress, the type and concentration of the contamination can be determined by chemical monitoring. Thus, as it was mentioned before, the best estimates integrate biological and chemical monitoring.

Various studies have been conducted to determine the effects of a broad range of xenobiotics on the biochemical, physiological and population structures of different types of fish and vertebrates. In these studies, the toxic rate of particular chemical combinations and their risk potential for the individuals of a species or ecosystem were determined, and some rapid biomarkers have been identified to diagnose contamination. Most current researches are based on the exploration of the response to stress at the cellular or molecular level, and the relationship between effects at the molecular level and populations (Depledge, 1994; Goksøyr, Solberg, & Serigstad, 1991; A. Lawrence & Poulter, 1998).

In addition to chemical pollutants, another aspect of such investigations is the study of benthic populations. Benthic ecologists have developed and expanded numerical indices that can be used to analyze and predict changes in features such as frequency, biomass, variety and benthic species combinations as a result of the pollutant changes (Bortone, 2005). Although the focus of marine environmental quality control is based on physicochemical and ecotoxicological studies and not much attention has been given to

biological variables, Dauer believes that biological criteria are one of the main components in determining the standards of water quality (Dauer, 1993).

Most researches indicate quantity model to evaluate ecological risk. According to this type of model, ecological risk assessment is estimated by obtaining the ratio between predicted environmental concentrations (PEC) and predicted no-effect concentrations (PNEC) (Mahmoud, 2010b). PNEC are calculated based on sediment or water quality guidelines that are widely applied to signify threshold concentration of chemical compounds and their biological effects on the population (Fdez-Ortiz de Vallejuelo, Arana, De Diego, & Madariaga, 2010; Hübner, Astin and Herbert, 2009; MacDonald, et al., 2003; Pekey, Karakaş, Ayberk, Tolun, & Bakoğlu, 2004; Thompson, Kurias, & Mihok, 2005)

In general, the basis of ERA is the estimation of the effects of chemical pollutants on populations, communities and ecosystems. Most techniques that are used to assess pollutant effects on the structure of benthic communities and chemical quality of sediments employ univariate and multivariate methods (Newman, Roberts, & Hale, 2002).

## **2.5. Environmental Impact Assessment**

As defined by the Council Directive, environmental impact assessment is assessment of the effects of specific public and private projects on the environment and it must determine the direct and indirect effects of a project on the following factors:

Human beings, the fauna, the flora, the soil, water, air, the climate, the landscape, the material assets and cultural heritage, and also clarify the interaction between these various elements. (Commission, 2010).

The significant environmental impacts including direct and indirect impacts that are categorized as follows:

- Impacts on human ;
- Use of natural and material resources, air and water;
- Impacts on ecology;
- Emissions of pollutants and waste removal;
- Assessment and forecasts of the effects of the usage natural resources, emissions or discharges, and waste;
- In the short to long term clarify indirect, cumulative, temporary, and permanent effects;
- Measures envisaged to avoid, reduce, or remedy adverse effects;
- An outline of optional solutions which have been studied before<sup>1</sup>.

Environmental impact assessments are necessary for any type of projects that may have significant effect on the environment (Rahimi and Mollaei, 2010).

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<sup>1</sup> (<http://www.esru.strath.ac.uk>)

### **2.5.1. Environmental Aspects and Impact Assessment**

An environmental aspect is an element of a facility's activities, products, or services which can or have interaction with the environment. Thus, the interactions and their effects on the environment may be uninterrupted in nature, temporary, or only associated with events, such as emergencies. While, the definition of an environmental impact is, any change to the environment, whether it is adverse or advantageous which is resulting from a facility's activities, products, or services and one of the changes can produce a significant environmental impact. The international standards ISO 14001 and 14042 is together accustomed to technically determine the concept, including how to determine environmental aspects for an organization or product, and how to find suitable analysis methods to assess performance due to these aspects, and how to improve it. (Australia, 2009; US.EPA, 2003; Vavra, Munzarova, Bednarikova and Ehlova, 2011).

For example, environmental aspect of discharges to stream is degradation of aquatic habitat and drinking water supply (US.EPA, 2003). There are many methods for identifying and prioritizing significant aspects and they are often depended upon estimations of environmental impact of different environmental aspects (WQPN, 2009).

The EPA provides a selected Techniques and Data Sources for clarifying and Evaluating Environmental Aspects and Impacts, which are shown in Fig. 2.2.

Techniques and Data Sources	When Best Used
Emission Inventories	Used to quantify emissions of pollutants to the air. Some data on emissions or chemicals of concern may already be available to you, based on EPCRA requirements and Clean Air Act (CAA) Title V permitting program data requirements.
Environmental Compliance Audits	Used to assess compliance with federal, state, and local environmental regulations. These methodologies are in common use. Their scope and level of detail vary. These are not typically directed at examining environmental impacts (particularly for products).
Environmental Cost Accounting	Used to assess the full environmental costs associated with activities, products, or services. Emerging protocols require comprehensive assessments to quantify such costs.
Environmental Impact Assessments	Used to satisfy requirements of the National Environmental Policy Act (NEPA) regarding the evaluation of environmental impacts associated with proposed projects. Methodology in common use, but not typically used to assess environmental impacts associated with existing operations.
Environmental Property Assessments	Used to assess potential environmental liabilities associated with facility or business acquisitions or divestitures. The scope and level of detail is variable. These assessments typically do not assess impacts associated with products or services.
Failure Mode and Effects Analyses	Commonly used in the quality field to identify and prioritize potential equipment and process failures as well as to identify potential corrective actions. Often used as a precursor to formal root cause analyses.
Life Cycle Assessments	Used to assess the cradle-to-grave impacts of products or processes, from raw material procurement through disposal. Life-cycle methodologies are somewhat subjective and can be resource intensive. These methodologies are described in ISO 14040-14048.
Pollution Prevention or Waste Minimization Audits	Used to identify opportunities to reduce or eliminate pollution at the source and to identify recycling options. Requires a fairly rigorous assessment of facility operations. These audits typically do not examine off-site impacts.
Process Flow Diagrams	Used to allow an organization to visualize and understand how work gets accomplished and how its work processes can be improved.
Process Hazard Analyses	Used to identify and assess potential impacts associated with unplanned releases of hazardous materials. Methodology in common use due to Occupational Safety and Health Act (OSHA) Process Safety Management regulations. Typically employs team approach to identify and rank hazards.
Project Safety/Hazard Reviews	Used to assess and mitigate potential safety hazards associated with new or modified projects. Methodologies in common use. Typically do not focus on environmental issues.
Risk Assessments	Used to assess potential health and/or environment risks typically associated with chemical exposure. Variety of qualitative and quantitative methodologies in common use.

**Table 2.9.** Selected Techniques and Data Sources for clarifying and Evaluating Environmental Aspects and Impacts (Extracted from US.EPA, 2003)

Thus, the growth of economy that is followed by a rapid expansion and development of industrialization under conditions of weak governmental regulation, can lead to the prominent and well-known consequences of rapid resource depletion, emission of hazardous gases, and air /water pollution. For example, in Taiwan, an impressive rate of economic growth due to enormous industrialization has leaded to serious water

contamination and air pollution, also in Venezuela there is an increasing degradation trend in inland waters because of the development of the petrochemical industry (Haque, 1999).

Effluents or discharges of industries which are normally discharged to the surrounded environment such as receiving waters require proper management to protect the environment and public health even after treatment. Because ,water pollution can have adverse effects on drinking water, fishing, tourism and other activities, so it may limit the future economic development (ARMCANZ, 1997) and (Alberta Environmental Protection (AEP), 1995). Thus, it is important to protect the environment and public health against the adverse effects of water pollution.

Impacts of the manufacturing and heavy industries accompanying with rapid rate of industrialization, increasing amounts of toxic and hazardous wastes that are being produced by a diversified amount of industrial activities. Petrochemical industries are one kind of the heavy industries and have undoubtedly been main factor and key drivers in the development of the complex and modern world that we live in. As the Petrochemical industries have been identified as important emission sources and point source of a wide range of chemical substances (Nadal, et al., 2011) , thus they have several impacts on the environment. For example, when industrial wastes are discharged pollutants (petroleum hydrocarbons, heavy metals, surfactants, toxins and/or salts), this may pollute the receiving waters (ambient water) and make them unsuitable as a water supply or cause a threat to aquatic organisms and aquatic life. Also, it can contaminate underground waters. Industrial wastewater can be categorized as follows: contaminated stormwater, cooling water, process waters and wash-down waters (WQPN, 2009).

Nowadays, the disposal of industrial effluents into natural water systems is a cause of serious environmental concern. Although petrochemical industries yield many benefits, their effluents can be considered more toxic than the oil refinery effluents (Wake, 2005). effluent is undoubtedly diluted within the receiving water and its scope depends on the size of the receiving water and the location of the outfall, intertidal or subtidal (Graham & Dorris, 1968).

Thus, the polluted effluent can have several adverse effects on the surrounded environment and the oil-polluted effluent can has impacts on marine aquatic organisms in different ways that can be listed as follows:

- It can kill them directly through coating and suffocation;
- Contact poisoning, or through exposure to water-soluble components;
- It can lead to the devastation of more sensitive juveniles and consequently eliminating populations;
- Oil has the potential of causing sub-lethal and stress effects, it can cause carcinogenic and mutagenic effects and also it can affect the behavior of individuals (Wake, 2005).

Aquatic ecosystems can be influenced by several factors such as climatic, geographic, physical, biological and human-induced factors; thus the effective management must combine site-specific information to expect a uniform set of guidelines to apply across all types of ecosystem and all regions. Thus the basis key drivers and the main factor of new approach to water quality management described in the new Water Quality Guidelines



(McAlpine & Humphrey, 2001). The Water Quality Guidelines provide wide range of cross reference to the general information which is provided in the Monitoring Guidelines. For example the Australian Guidelines for Water Quality Monitoring and Reporting (the Monitoring Guidelines) contains information on the practical designing monitoring programs, collecting and analyzing data for the measurement of water quality (ARMCANZ & ANZECC, 2000). There are several guidelines for effluent management and quality such as, Canadian Council of Ministers of the Environment(CCME, 1999; MacDonald et al., 2002) and US.EPA (US.EPA, 1995; US. EPA New England, 2010). The summary of effluent limits and end-of-pipe discharge standards for sewage wastewater are shown in Table 2.10 and 2.11.

**Table2.10.**Effluent limits (US.EPA, 1995; US EPA New England, 2010)

No.	Parameter	Effluent Limit	Limit type based on
1	Acenaphthylene	100000 ng l-l	daily maximum
2	Acenaphthene	100000 ng l-l	daily maximum
3	Anthracene	100000 ng l-l	daily maximum
4	Benzo(a)anthracene	3.8 ng l-l	daily maximum
5	Indeno(1,2,3-cd) Pyrene	3.8 ng l-l	daily maximum
6	Chrysene	3.8 ng l-l	daily maximum
7	Benzo (b) fluoranthene	3.8 ng l-l	daily maximum
8	Benzo (k) fluoranthene	3.8 ng l-l	daily maximum
9	Benzo (g,h,i) perylene	100000 ng l-l	daily maximum
10	Dibenzo (a,h) anthracene	3.8 ng l-l	daily maximum
11	Benzo (a) pyrene	3.8 ng l-l	daily maximum
12	Fluoranthene	100000 ng l-l	daily maximum
13	Phenanthrene	100000 ng l-l	daily maximum
14	Pyrene	100000 ng l-l	daily maximum
15	Fluorene	100000 ng l-l	daily maximum
16	Naphthalene	20000 ng l-l	daily maximum
17	Total Group I Polycyclic Aromatic Hydrocarbons (PAH)1	10000 ng l-l	daily maximum
18	Total Group II Polycyclic Aromatic Hydrocarbons (PAH)2	100000 ng l-l	daily maximum
19	Total Petroleum Hydrocarbons (TPH)	5.0 mg/l	daily maximum

1: Group I PAHs: a. Benzo(a) Anthracene, b. Benzo(a) Pyrene, c. Benzo(b)-Fluoranthene, d. Benzo(k)Fluoranthene, e. Chrysene, f. Dibenzo(a,h) Anthracene, g. Indeno(1,2,3-cd) Pyrene

2: Group II PAHs: a. Acenaphthene, b. Acenaphthylene, c. Anthracene, d. Benzo(ghi)-Perylene, e. Fluoranthene, f. Fluorene, g. Naphthalene, h. Phenanthrene, i. Pyrene

**Table2.11.** End-of-pipe discharge standards for sewage wastewater

No.	Parameter	Effluent Limit	Limit type based on
1	Total Petroleum Hydrocarbons (TPH) <sup>1</sup>	10 mg/l	Daily maximum
2	Total Oils & Greases <sup>1</sup>	10 mg/l	Daily maximum
	Total Oils & Greases <sup>2</sup>	10 mg/l	Maximum Allowable Standard
3	Total Organic Carbon <sup>1</sup>	110 mg/l	Daily maximum
	Total Organic Carbon <sup>2</sup>	75 mg/l	Maximum Allowable Standard
4	pH <sup>1</sup>	6.5 to 8.5	Daily maximum
	pH <sup>2</sup>	6-9	Maximum Allowable Standard
5	Total Suspended Solids (TSS) <sup>1</sup>	100 mg/l	Daily maximum
	Total Suspended Solids(TSS) <sup>2</sup>	50 mg/l	Maximum Allowable Standard
6	Temperature <sup>2</sup>	35 °C	maximum
7	Turbidity <sup>2</sup>	75 NTU	Maximum Allowable Standard
8	Chemical Oxygen Demand <sup>2</sup>	100 mg/l	Maximum Allowable Standard
9	Dissolved Oxygen <sup>2</sup>	> 3 mg/l	Maximum Allowable Stand
10	Total Dissolved Solids <sup>2</sup>	1,500 mg/l	Maximum Allowable Stand

1. (UWI, 2004) 2.(EHS, 2010)

According to the definition of EIA "the systematic evaluation of the potential adverse and beneficial environmental effects of a proposed development or activity" (EC., 2004; EC. ,2010), also at the end of the project, an EIA should be followed by an audit (Cojocariu , Vunk , Kjemperud, Dancette, 2004). Therefore, in this study, rate of concentration and pollutant load factor are used and they are compared with the guidelines to determine and assess the environmental aspect of the PETZONE wastewater and its environmental impacts. Moreover, the concentration of the selected factors were assessed in the sediments around the PETZONE and the ecological risk assessment (ERA) were determined to clarify the environmental health status (EHS) of this valuable aquatic environment and the adverse effects of thee PETZONE petrochemical industries on it.

## CHAPTER III: MATERIALS AND METHODS

### 3.1 Sampling and Field Work

#### 3.1.1. Musa Bay

Sediment samples from Musa Bay were collected from 12 stations located in the coastal area of the PETZONE from June 2009 to June 2010, by using an Ekman-Birge grab sampler 225 cm<sup>2</sup> (all of the sediment samples were prepared during 4 times sampling, at low tide with 3 replicate).

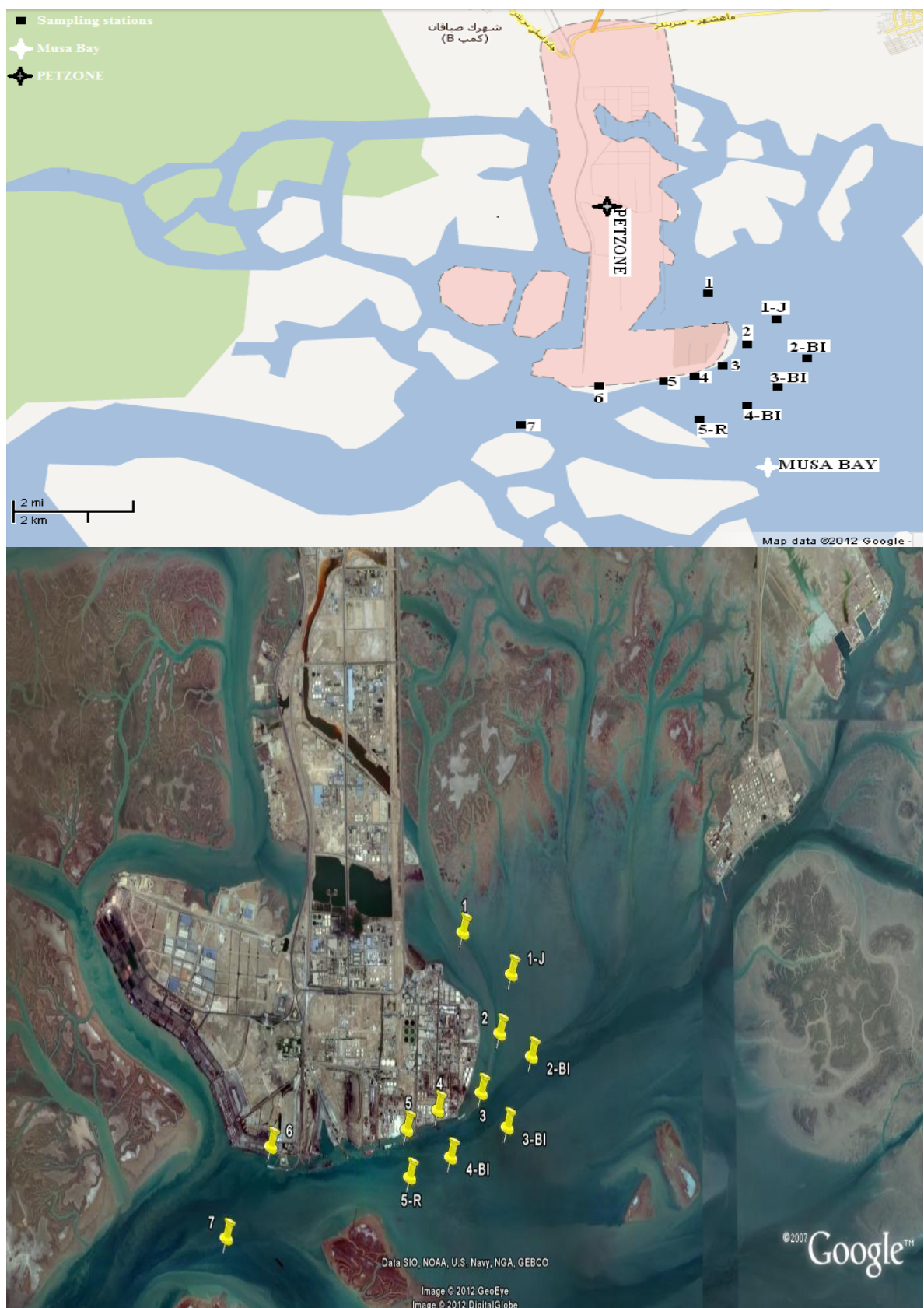
All the sampling stations were determined based on the suggestions of the experts of PETZONE environmental office. Five sampling stations (sampling stations: 1, 2, 3, 4 and 5) were in the proximity of PETZONE wastewater discharge points and make another sampling point whit 700 m apart on each transect (sampling stations: 1-J, 2-BI, 3-BI, 4-BI and 5-R). Station 6 was determined based on its closeness to the Aluminium port of Bandar-e- Imam Khomeini (which is one of the main ports in this area). Also station 7 is located in the Mouth of Marimos creek which has a high water depth, high water circulation and it is somehow far from the PETZONE coastal area. In general, 12 sampling stations were monitored and they are represented as Table 3.1. Also, the sampling sites are shown in Figure 3.1.

**Table3.1.** Sampling stations of Musa Bay study

Station No.	Station name	E	N
<b>1</b>	Junction of Jafari & Zangi Creeks	49° 6'48.50"E	30°26'53.50"N
<b>1-J</b>	700 m from the junction of Jafari & Zangi Creeks	49° 7'29.49"E	30°26'36.12"N
<b>2</b>	BI-PC* East Pond	49° 7'12.44"E	30°26'17.34"N
<b>2-BI</b>	700 m from BI-PC East Pond	49° 7'40.01"E	30°25'59.60"N
<b>3</b>	BI-PC South East	49° 7'0.47"E	30°25'50.09"N
<b>3-BI</b>	700 m from BI-PC South East	49° 7'28.11"E	30°25'28.77"N
<b>4</b>	BI-PC Aromatic	49° 6'26.87"E	30°25'37.39"N
<b>4-BI</b>	700 m from BI-PC Aromatic	49° 6'45.47"E	30°25'11.46"N
<b>5</b>	Razi	49° 6'2.06"E	30°25'29.16"N
<b>5-R</b>	700 m from Razi	49° 6'12.26"E	30°25'1.02"N
<b>6</b>	MUSA1	49° 4'17.99"E	30°25'20.64"N
<b>7</b>	MUSA2	49° 3'39.19"E	30°24'38.17"N

\*BI-PC: Bandar-e-Imam Khomeini petrochemical company

The study area is covered with fine-grained sediments and the top surface sediment 0-5 or 0-10 cm from each grab samples. Then, sediment samples were stored in aluminum foils and placed on compartment ice after sampling, immediately transported to the laboratory and kept in the refrigerator at -20 °C until further analysis for measuring organic contaminants (TPH and PAHs), total organic carbon (TOC), and grain size. This follows the methodologies by Paul et al. (1992) and MOOPAM (1999).



**Fig.3.1.** Sampling stations in Musa Bay (extracted from Google map -2012)



**Fig.3.2.** sediment sampling from the Musa Bay

### **3.1.2. Petrochemical Special Economic Zone (PETZONE)**

Wastewater samples within PETZONE were collected from 18 stations from June 2009 to June 2010 (every 3 months- from June 2009 to June 2010 - 4 times sampling in the PETZONE with three replicate). The sampling sites are shown in Figure 3.7 and the sampling stations are labeled in Table 3.2. Wastewater samples were collected in 1000 ml amber glasses, placed on to ice compartments after sampling and transported to the laboratory immediately for further analysis of the TPH and PAHs and also Chemical Oxygen Demanded (COD), according to American Public Health Association (APHA,1998) and (MOOPAM, 1999).

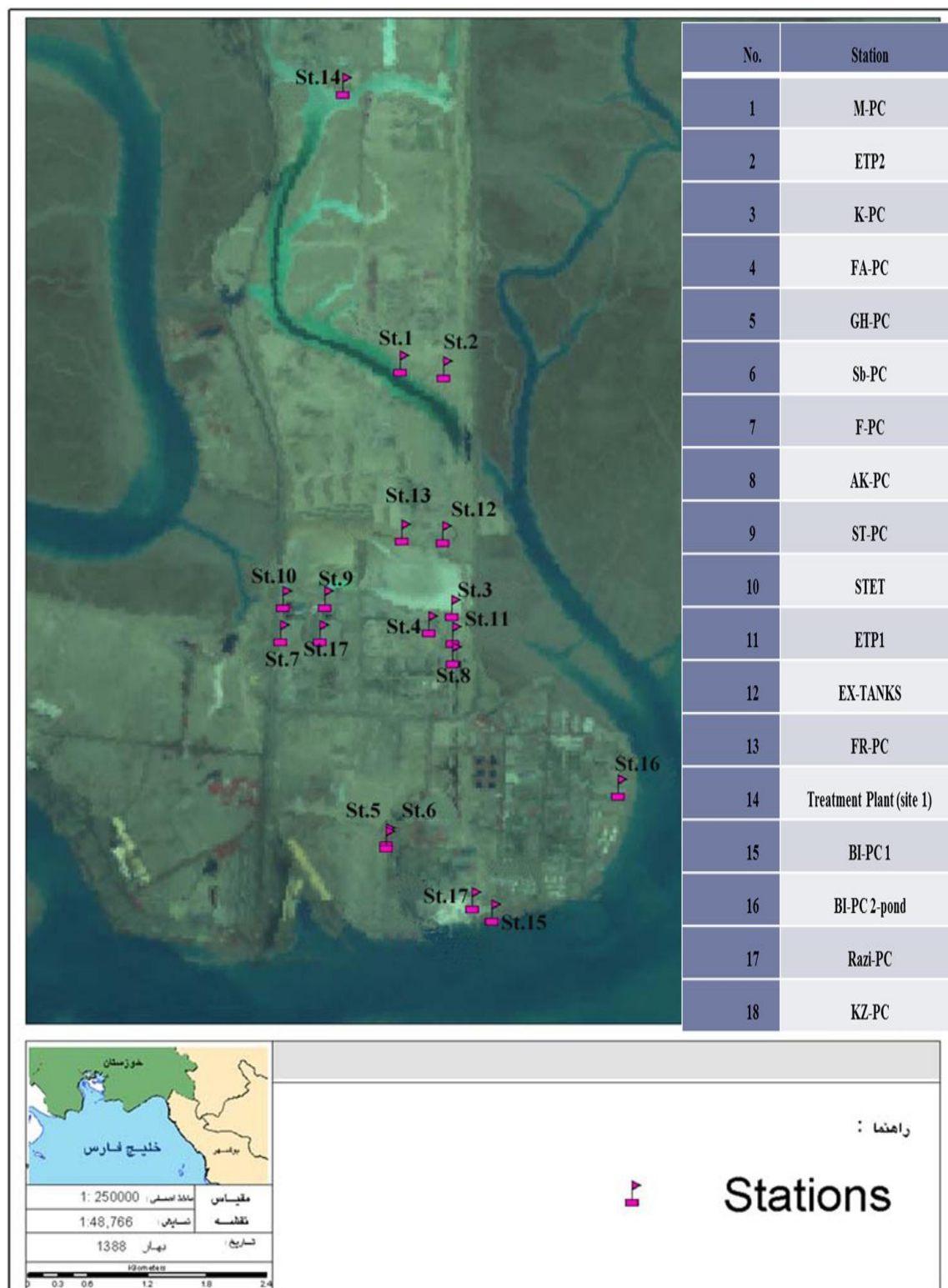


**Table 3.2.** Location of sampling stations inside the PETZONE

No.	Station	Full name	N	E
1	M-PC	Marun petrochemical company	30° 28' 37.7"	49° 05' 32.6"
2	ETP2	Effluent treatment plant 2	30° 28' 36.0"	49° 05' 49.0"
3	K-PC	Karoon petrochemical company	30° 30' 1.6"	49° 05' 16.9"
4	FA-PC	Fanavaran petrochemical company	30° 27' 41.5"	49° 05' 49.8"
5	GH-PC	GHadir petrochemical company	30° 27' 41.7"	49° 05' 34.5"
6	Sb-PC	Shimi Baft petrochemical company	30° 27' 45.1"	49° 05' 17.9"
7	F-PC	Fajr petrochemical company	30° 27' 19.5"	49° 04' 5.7"
8	AK-PC	Amir Kabir petrochemical company	30° 27' 7.9"	49° 04' 49.2"
9	ST-PC	Shahid Tondgooyan petrochemical company	30° 27' 8.4"	49° 05' 54.1"
10	STET	Shahid Tondgooyan Effluent treatment plant 1	30° 27' 17.1"	49° 05' 53.8"
11	ETP1	Effluent treatment plant 1	30° 27' 11.6"	49° 05' 45.3"
12	EX-TANKS	Export Tanks	30° 26' 1.4"	49° 05' 30.4"
13	FR-PC	Farabi petrochemical company	30° 25' 47"	49° 06' 42"
14	Treatment Plant (site 1)	1 <sup>st</sup> Site Treatment Plant	30° 27' 12"	49° 05' 59"
15	BI-PC 1	Imam Khomeini petrochemical company1	30° 30' 36.9"	49° 06' 10.9"
16	BI-PC 2-pond	Imam Khomeini petrochemical company2	30° 26' 19"	49° 07' 0.21"
17	Razi-PC	Razi petrochemical company	30° 25' 40.8"	49° 06' 3.3"
18	KZ-PC	Khouzestan petrochemical company	30°27' 11.86"	49°04' 44"



**Fig.3.3.** Wastewater sampling from the selected effluents samples (inside the PETZONE)



**Fig.3.4.** Sampling stations inside the PETZONE



## **3.2. Experimental Methods**

### **3.2.1. Sediment Quality Analysis**

#### **3.2.1.1. Total Petroleum Hydrocarbon and Polycyclic Aromatic Hydrocarbons**

In the laboratory, 20 grams of freeze-dried sediment sample (freeze-drier model: Operon), ground and sieved at 125  $\mu\text{m}$ , are put in the glass tube of the reactor. The extraction was conducted using a microwave oven (ETHOS one- temperature 115°C, 20 min).

A fifteen gram aliquot of the freeze-dried sediment sample was put in the glass tube of the reactor with 40 ml of hexane:methylene chloride (1:1v/v). Sulfur was removed using activated elemental copper in order to avoid potential interferences during gas chromatography, and the extracts were concentrated using a rotary evaporator. Sediment samples were fractionated on a silica gel-alumina column and the column of systems contained 10 ml of silica powder, 10 ml hydrated alumina, 1-2 grams of sodium sulphate. After passing the extract through the system, the extract was placed in 5 ml vials and then the extract was dried with anhydrous sodium sulfate and transferred in a graduated tube and concentrated down to 1 to 2 ml using a flow of clean nitrogen. Individual PAHs were quantified based on the retention time with a reliable PAHs mixed standard (Sigma), and concentrations of each PAH were calibrated based on the standard calibration curve. Finally, the concentration of the following PAHs were determined: six low molecular weight, two and three rings aromatics namely, Naphthalene (Na), Acenaphthylene (Acpy) , Acenaphthene(Acp), Fluorene (Flur), Phenanthrene (Phen) and Anthracene (Ant), and 10 high molecular weight, four, five and six aromatic rings namely, Fluoranthene (Flu),

Pyrene (Py), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene(BbF), Benzo(k) fluoranthene (BkF) , Benzo (a) pyrene (BaP), Dibenzo(a,h)anthracene (DbahA), Benzo (g,h,i) perylene (BghiP), Indeno (1,2,3-cd) pyrene (IP) (Viguri, et al., 2002; Herzfelder & Golledge, 2004; Semlali , Chafik, Talbi & Budzinski,2012).



Fig.3.5. Laboratory analysis of the sediment samples

In addition, compound concentrations below detection limits were assumed to be zero for the  $\Sigma$ PAHs in each sample. Method blanks (solvent) and spiked blanks (standards spiked into solvent) were routinely analyzed with field samples (wastewater and sediment samples). Initially, each sample was analysed for total petroleum hydrocarbons using an UV fluorescence (UVF- 2500- fixed excitation wavelength :310 nm; the emission

wavelength : 360 nm ) and gas chromatography mass spectrometry (GC-MS; GC, Agilent, 6890N, MS: Agilent, 5973N) for PAHs ( MOOPAM, 1999; De Mora et al., 2010b).

### **3.2.1.2. Total Organic Carbon and Other Parameters**

The ignition of loss method (IG) for determining organic and carbonate carbon was used to determine the percentage of total organic matter by weight loss in the ignition (in 550°). It was performed by weight difference after calcination at 500°C (difference between the first weight and the dry weight) (Schulte & Hopkins, 1996).

Moreover, the grain size of sediment samples was determined by the sieve method based on Holme & McIntyre (1984). At the first, a dispersed and homogeneous suspension was prepared which was diluted with 0.5% sodium hexametaphosphate to 1000 ml and it was sieved through the following meshes: 2, 1, 0.5, 0.125 and 0.063 mm.

TOC and nitrogen was measured in surface sediment by using a Perkin-Elmer 2400 carbon–hydrogen–nitrogen–sulfur (CHNS) elemental analyzer at 950°C combustion temperature. Two g of freeze-dried sediment sample was treated with an HCL (10%) solution in a specific container to remove the inorganic carbon and was dried overnight at 60°C. A 5 to 15 mg of each sample was put into a tarred 5.8-mm silver capsule, which was compressed with tweezers for CHNS analysis. The percent of organic carbon was measured in duplicate.

### 3.2.2. Wastewater Quality Analysis

#### 3.2.2.1. Total Petroleum Hydrocarbon and Polycyclic Aromatic Hydrocarbons

In the laboratory, according to US. EPA Method 1664A for extracting oil and grease from water, the liquid-liquid extraction (LLE) with a separatory funnel as the means, was used for extraction. According to this method each sample was extracted in normal hexane (n-hexane) as the extraction solvent. The mixture was shaken vigorously for 2 minutes and the upper layer of the solvent was separated (remaining parts were extracted by 2 portions of 30 ml n-hexane). In addition, anhydrous  $\text{Na}_2\text{SO}_4$  was added to each extracted sample to absorb the traces of water and the combined extracts in a tarred distilling flask, and then a rotary-evaporator was used to release the solvent and decrease the volume of the extracts (U.S.EPA, 1999b)



Fig.3.6. Laboratory analysis of the wastewater samples

Extracted samples were fractionated on a silica gel-alumina column (silica gel grade 60, neutral alumina- Merck; 20 mm diameter column containing from top 10 g silica gel (3% deactivated) and 15 g alumina (6% deactivated); sample eluted with 175 mL of dichloromethane (DCM)/hexane (50:50, v:v); also 1-2 grams of sodium

sulphate. After passing the extract through the system, the extract was placed in 5 ml vials and dried with anhydrous  $\text{Na}_2\text{SO}_4$  and transferred in a graduated tube and concentrated down to 1 to 2 ml using a flow of nitrogen ( $\text{N}_2$ ). Individual PAHs were quantified based on the retention time with a reliable PAHs mixed standard (Sigma), and concentrations of each PAH components were calibrated based on the standard calibration curve.

Finally, the concentration of the following PAHs were determined: six low molecular weight, two and three rings aromatics namely, Naphthalene (Na), Acenaphthylene (Acpy), Acenaphthene(Acp), Fluorene (Flur), Phenanthrene (Phen) and Anthracene (Ant), and 10 high molecular weight, four, five and six aromatic rings namely, Fluoranthene (Flu), Pyrene (Py), Benzo(a)anthracene (BaA) , Chrysene (Chr), Benzo(b)fluoranthene(BbF), Benzo(k) fluoranthene (BkF) , Benzo(a)pyrene (BaP), Dibenzo(a,h)anthracene (DbahA) , Benzo (g,h,i) perylene (BghiP) and Indeno (1,2,3-cd) pyrene (IP) ( Viguri, et al., 2002; Herzfelder & Golledge, 2004; Semlali, et al., 2012).

After extraction, each sample was initially analyzed for total petroleum hydrocarbons by UV fluorescence (UVF- 2500- fixed excitation wavelength :310 nm; the emission wavelength : 360 nm ) and gas chromatography mass spectrometry (GC-MS; GC, Agilent, 6890N, MS: Agilent, 5973N) for PAHs (De Mora, et al., 2010b; ROPME, 1999a; US.EPA).

The condition of gas chromatography mass spectrometry (GC-MS; GC, Agilent, 6890N, MS: Agilent, 5973N), during the analysis (wastewater / sediment), was as follows:

## GC

Injector Temp: 270°C, interface Temp : 280 °C , He, 1/5 ml/min

Oven Temp program: 60 °C (1 min)  $\xrightarrow{3^{\circ}\text{C/min}}$  100° C  $\xrightarrow{4^{\circ}\text{C/min}}$  285 ° C (10 min)

Column: Hp- 5 ms, 0/25 mm  $\times$  30m  $\times$  0/25  $\mu$ m

Injection volume: 1  $\mu$ li

## MS

Ion source: 230 ° C

Ionization mode: electron impact

Electron energy: 70 ev

EM Voltage: 2000 V

Monitoring mode: SIM (Single Monitoring)

Ions monitoring: 152,153,166,178,202,228,252,276,278

Quantitation: external method

### 3.2.2.2. Chemical Oxygen Demand and Other Physical Parameter

Chemical oxygen demand (COD) is the quantity of oxygen that is produced by all organic matter that presents in water or wastewater sample (it means both biodegradable organic matter by micro-organisms in biochemical and non-biodegradable materials in chemical process). In this study, the COD analysis was based on the dichromate method which is very applicable for monitoring wastewaters (wastewater treatment systems). In this method, the oxidant agent is dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) which was performed under controlled condition, potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) in the presence of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) for a fixed period (usually two hours) with silver sulphate ( $\text{Ag}_2\text{SO}_4$ ) as catalyst (by WTW Thermoreactors- CR 2200 which is the routine instrument for the digestion reactions for the analysis of wastewater). Finally, COD was calculated by titrating (Gonzalez, 1996; Liang, Wang, Zhou, & Liu, 2009).

Other physical parameters such as electrical conductivity (EC), total dissolved solids (TDS), pH, temperature, and dissolved oxygen (DO) were measured in the field by using:

- Dometer- Inolab oxi Level2- WTW- GmbH & Co. KG, Germany.
- pHmeter – pH597- WTW- GmbH & Co. KG, Germany.
- Conductivity Meter – LF197-WTW- GmbH & Co. KG, Germany.

### **3.2.3 Biodiversity and Richness**

In 2000, the WFD (European Water Framework Directive) maintained and defined the concept of ecological quality in assessments aimed at determining water quality. Such assessments have been conducted based on the combination and frequency of different biological elements of an ecosystem (such as phytoplankton, benthos organism and fish), along with the physical and chemical factors and related hydro-morphological indices (EC, 2000).

When the environmental pollutant is present, the species richness and body size of the individuals decreases, whereas the number of all the individuals, compression and biomass of the opportunist species increases (Pearson & Rosenberg, 1978). Also the invertebrate organisms that have long lives with different life cycles, will response variably to anthropogenic stresses (Kitsiou & Karydis, 2011).

As the biodiversity study is an essential part of the environmental assessment, there are several indices and models to measure diversity, thus it is difficult to choose the best method for estimating and assessing the biodiversity; for example Shannon-wiener Index,

Pielou evenness Index, Berger-Parker Index and Simpson Index. A scientific method to use when selecting a diversity index is to make the decision on the basis of whether it has the ability to fulfill certain function criteria to distinguish between study sites, dependence on sample size, what component of diversity is being measured, and whether the index is widely used and understood (Vollenweider et al., 1992). In the present study, Shannon–Wiener Index was used to assess the diversity of benthic organism which is a regular and simplified method for comparing diversity between different ecosystems. This index is based on random sampling (usually based on density) and assumes that all the species are represent in the sample.

The index is:

$$H' = -\sum p_i \log_2 p_i, \text{ and } p_i = n_i/N.$$

(  $n_i$ : number of individuals of the  $i_{th}$  species /  $N$ : total number of individuals) (Shannon & Weaver, 1963; Jørgensen, et al., 2005; Gray, 2000; Clarke & Warwick, 2001).

The value of index can take between 0 and 5. According to the literature (Vollenweider et al., 1998), low index values are considered to be indications of contamination.

- 1- High status: Greater than 4 bits/individual
- 2- Good status: 4 to 3 bits/individual
- 3- Moderate status: 3 to 2 bits/individual
- 4- Poor status: 2 to 1 bits/individual
- 5- Bad status: 1 to 0 bits/individual



Benthic samples from Musa Bay were collected from 12 stations located in the coastal area of the PETZONE from June 2009 to June 2010, by using an Ekman-Birge grab sampler (225 cm<sup>2</sup> - every 3 months, at low tide). For the study of macrobenthos, samples were immediately sieved through a 0.5 mm mesh screen and samples were treated with rose Bengal and benthic organisms were removed and separated according to the lower animal taxonomic groups; also, all of the benthic organisms were counted and their wet weight was recorded for each *taxon*. Finally, abundance (number of individuals per m<sup>2</sup>), Biomass (g/m<sup>2</sup>), diversity (Shannon-Wiener H') index were calculated.

#### **3.2.4. AZTI Marine Biotic Index (AMBI)**

The AZTI Marine Biotic Index (AMBI) was introduced by Borja et al. (2000) to assess and determine the qualitative effects of sediment conditions on the benthic communities of soft and muddy marine sediments. This index was then utilized to assess different effects and sources of stress. The advantage of this index was demonstrated by the diagnosis of exceptional effects in the impacted area. Based on this index, benthic community is classified according to their sensitivity to increasing stress (Borja, Muxika, & Franco, 2003a) (Table 3.3).

The benthic organisms were divided into 5 ecological groups GI, GII, GIII, GIV and GV which are categorized based on their sensibilities and their responses to anthropogenic stresses (Borja, et al., 2000). Based on AMBI formula, its scale ranges between 0-7 (Table 3.4).

$$AMBI = \frac{(0 \times GI\%) + (1.5 \times GII\%) + (3 \times GIII\%) + (4.5 \times GIV\%)}{100}$$

*GI*: Very sensitive species to pollutant and present under unpolluted condition;

*GII*: Species indifferent to excess of enrichment;

*GIII*: Species tolerant to excess of organic matter enrichment;

*GIV*: Second-order opportunist species, mainly small sized polychaetes;

*GV*: first- order opportunist species, essentially deposit-feeders.

**Table 3.3.**AMBI classification

AMBI	M-AMBI	Disturbance Classification	Ecological group	Ecological Quality Status ( WFD)
<b>0.0&lt;AMBI≤1.2</b>	> 0.82	Unpolluted	I -II	<b>High Status</b>
<b>1.2&lt;AMBI≤3.3</b>	0.62-0.82	Slightly polluted	III	<b>Good Status</b>
<b>3.3&lt;AMBI≤5</b>	0.41-0.61	Moderately polluted	IV-V	<b>Moderate Status</b>
<b>5.0&lt;AMBI≤6</b>	0.21-0.4	Heavily polluted	V	<b>Poor Status</b>
<b>6.0&lt;AMBI≤7.0</b>	<0.2	Extremely polluted	-	<b>Bad Status</b>

- : without organisms

### 3.2.5 Multivariate- AMBI- M-AMBI<sup>1</sup>

The usage of AMBI and M-AMBI are in benthic quality assessments but M-AMBI is a multivariate tool which combines AMBI, richness and Shannon diversity in the assessment (Borja, Muxika, & Rodríguez, 2009). This method compares monitoring results with reference condition by salinity stretch, for estuarine ecosystem, in order to derive an

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<sup>1</sup> The software can be freely download from website: <http://www.azti.es>

ecological quality ratio. The final values determine the relationship between the observed values and reference condition value (values are ranged between 0 and 1) (Vincent, Heinrich, Edwards, Nygaard, & Haythornthwaite, 2002; Pinto, et al., 2009).

This index can determine the anthropogenic pressures in marine environment, because it has been used in several examinations and in different geographical sites (Borja, et al., 2000; Muniz, Venturini, Pires-Vanin, Tommasi, & Borja, 2005).

### 3.2.6. Sediment Quality Assessment

Based on the physical properties of PAHs, the majority of PAH components are high-molecular-weight PAHs and pose minimal risk of mobilization and transport through the environment; however, the low-molecular-weight PAHs are more easily transported through the environment (ATSDR, 1995). In this study the PAH isomer ratio was used to infer the possible anthropogenic sources of PAH from the natural source. These ratio and their classification was defined in Table 3.4 (Yunker, et al., 2002; Budzinski et al., 2004; Zhang et al., 2004; Wang, Wang, He, Du & Sun, 2011)

**Table 3.4.** PAH isomer pair ratio measurement

PAH isomer	ratio	Source
<b>Anthracene/anthracene+phenanthrene</b>	< 0.4	Petroleum
	0.4-0.5	Petroleum combustion
	>0.5	Dominance of Combustion of coal
<b>Benzo(a)anthracenen/Benzo(a)anthracenen+chrysene</b>	<0.10	Petroleum input or diagenetic sources
	>0.1	Characteristic of combustion processes
<b>Fluoranthene/ Fluoranthene + pyrene</b>	<0.20	Petroleum
	0.20-0.35	Petroleum and combustion
	>0.35	Combustion
<b>Indeno (1,2,3-cd) pyrene / Indeno (1,2,3-cd) pyrene + Benzo (g,h,i) perylene</b>	< 0.2	Fom petroleum origin input
	0.2 -0.5	mainly from oil combustion)
	>0.5	mainly from coal, wood and grass combustion

### 3.3. Ecological Risk Assessment

Ecological risk assessment was performed to assess adverse biological effects or the degree of toxicity of these pollutants in the sediment. In this study, the ecological risk was assessed based on the concentration of PAHs in the sediments and the sediment quality guidelines (SQGs) were used to assess adverse biological effect of TPH in this area (Hübner, et al., 2009; Khairy, et al., 2009).

This (SQGs) method indicates that the relationship between the concentrations of contaminants in sediment samples and adverse biological effects is based on the specific values of effect range low or threshold effect level (TEL) and effect range medium or probable effects level (PEL). The TEL value has been estimated as the concentration of contaminants with a relatively low effect on biological communities, and PEL is a concentration of contaminants with high toxic effects. Occasional toxic effects are expected to occur from contaminants Concentrations between TEL and PEL occasional toxic effect are expected (Long, MacDonald, Smith, & Calder, 1995; Long & Morgan, 1990 Hübner et al., 2009;).

In 1996, the TPH concentration in the Persian Gulf sediments was categorised into four levels (guideline) and the natural background level ( $<15 \mu\text{g/g}$ ) was determined in the Gulf (the natural background value can be considered as TEL and  $500 \mu\text{g/g}$  as PEL) (Massoud et al., 1996).

The overall toxicity of TPH was estimated by PEL quotients (PELq's). The PELq factor is the average of the ratios between the concentration of these parameters the sediment sample and the related PEL value (Alvarez-Guerra,, Viguri, Casado-Martinez, &

DelValls, 2007; Fdez-Ortiz de Vallejuelo, Arana, 2008). This factor describes contamination effect on biological organisms in sediment which range as non-adverse effect ( $PELq < 0.1$ ), slightly adverse effect ( $0.1 < PELq < 0.5$ ), moderately effect ( $0.5 < PELq < 1.5$ ) and heavily effect ( $PELq > 1.5$ ) (Vallejuelo, Arana, Diege, & Madariaga, 2010).

Also the sources of PAHs were identified by employing the ratios of specific PAHs compounds and principal component analysis (PCA) (Kitsiou & Karydis, 2011). Furthermore, the ecological risk was assessed based on the concentration of PAHs by using the Hakanson method as follows (Hakanson, 1980; El- Said & Youssef, 2012):

- Contamination factor (which is used to evaluate the environmental pollution by single substances) was calculated. This factor can also take into consideration different toxicities and it can be measured by the following equation (Westernhagen, Cameron, Dethlefsen, & Janssen, 1989; Hakanson, 1980; Loska, Cebula, Pelczar, Wiechula, & Kwapuliński, 1997; Meng, Qin, Zheng, & Zhang, 2008).

$$C_f^i = C_{0-1}^i / C_n^i$$

In this study,  $C_{0-1}$ , is the average concentration of PAHs in the sampling sediments and  $C_n$ , is the concentration of PAHs in natural sediments (guideline value: 4022 ng/g (Long, et al., 1995)). This factor was ranged in four categories:

- low  $C_f < 1$ ,
- moderate  $1 \leq C_f < 3$ ,
- $3 \leq C_f < 6$  as considerable
- $C_f > 6$  as very high (Hakanson, 1980).

- Bioproduction (BPI) was calculated based on the relation between nitrogen (mg/g) and the percentage of organic matter. And the equation of toxic-response factor ( $T_r$ ) according to Hakanson Method is:

$$- T_r = \frac{S_t \times BPI}{5}; \text{ (Sedimentological-toxic factor } (S_t) \text{ is 40 for PAHs);}$$

- Based on this method, the Risk Index (RI) value is,

$$RI = T_r \times C_f$$

- Finally, the Sedimentological-toxic ( $S_t$ ) factor is 40 for PAHs and it is the basic level for calculation for RI. Therefore, potential ecological risk index for the aquatic area was determined based on following terminology:

- Low ecological risk  $RI < 50$ ;
- Moderate ecological risk  $50 \leq RI < 100$ ;
- High ecological risk  $100 \leq RI < 200$ ;
- Very high ecological risk  $RI > 200$  (Hakanson, 1980).

### **3.4. Identifying the Environmental Aspects and Determining the Environmental Impacts**

The meaning of environmental quality is “safe drinking water, healthy ecosystems, safe food, toxic-free communities, safe waste management, and the restoration of contaminated sites“ (Bowen, 2002). The ISO 14000 is a series of standards determining a systematic and organized approach to environmental management which emerged as a result of the GATT <sup>1</sup> negotiations and the 1992 Rio de Janeiro summit on the environment. In 1992, the British Standards Institution (BSI) introduced BS7750, which is the first world's environmental management standards (EMS) and other countries developed their own EMS based on it (Alan, Ofori, & Briffett, 1999). In 1996, The ISO 14000 series of standards were first published and it covered:

- Environmental management systems;
- Environmental auditing;
- Environmental performance evaluation;
- Environmental labeling;
- Life-cycle assessment;
- Environmental aspects in product standards.

The revised ISO 14001:2004 and ISO 14004:2004 standards were published in 2004; with ease of understanding, more understandable requirement intent, an emphasis on conformance, and compatibility with ISO 9000:2000 (Haider, 2010).

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<sup>1</sup> Uruguay round of the General Agreement on Tariffs and Trade

This is more focused on environmental performance which is “measurable results of an organization’s management of its environmental aspects”(Hiew, 2010).

Thus, according to ISO 14000, each project (new project) has various potential sources of risk and one of them is environmental risk which may arise from the interaction between the project and surrounding environment (including air, water, land, plants and wildlife). Environmental Risk Assessment covers the risk to all types of ecosystems and it contains key stages including: Hazard identification (which is the inherent potential for something to cause harm), Identification of consequences- if the hazard was to occur, estimation of the magnitude of the consequences, estimation of the probability of the consequences (exposure assessment or consequence assessment) and evaluating the significance of a risks (EHSC, 2008).

Therefore, Environmental Impact Assessment includes an extensive field which contains all activities that attempt to analyze and evaluate the effects of human stresses on natural and anthropogenic environments (Suter , Barnthouse & O'Neill, 1987; Mustafa & Al-Bahar, 1991).

Basically, risk assessment and risk management is a subjective process (Dickson, 2001), but the basic principles and the key stages of the processes are basically same in each case study (Defra, 2002; EHSC, 2008).

The risk can be assessed based on qualitative approaches (ranking methods) such as Fine’s method which uses the risk score and brings out the relationships between the consequences of an accident (C), the level of exposure (E) and the probability (P). The risk score provides a mechanism for ranking various risks. In qualitative risk assessment



approaches, the meaning of high, medium, low and very low can be determined in various ways; for example using a descriptive or numerical scale, or often based on expert judgment (EHSC, 2008). For example: the matrix in qualitative risk assessment can be defined as follows:

Probability of receptors being exposed↑	High	Medium risk	Medium risk	High risk	High risk
	Medium	Low risk	Medium risk	Medium risk	High risk
	Low risk	Low risk	Low risk	Medium risk	Medium risk
	Very low	Very Low risk	Low risk	Low risk	Medium risk
		Very low	Low risk	Medium	High
		Consequences of hazard being realized →			

Several equations were determined for assessing the environmental impact For example a simpler version of evaluation is:

$$\text{Environmental impact} = \text{Severity} \times \text{Frequency};$$

This equation is varied in different organization and some of them use a more complex method. Moreover, each impact has its own tolerance limits and ranges; therefore depending on the type of pollution, the severity is defined differently. In addition, the frequency explains the amount of time that the pollutants are discharged into the environment (Carpenter, 1995).

In this study the effluent quality of selected petrochemical companies of PETZONE was monitored approximately every two months and assayed for petroleum hydrocarbon pollution, and their environmental impacts and aspects was evaluated based on ISO 14001:2004 and also abovementioned equation (Carpenter, 1995).

In this research, the method for the analysis of environmental impact assessment was carried out as follows:

- 1- The aspect is : Total petroleum hydrocarbon and PAHs disposal (from the effluents of PETZONE petrochemical companies);
- 2- Impact: water pollution.

Thus the terminology based on the sensitivity of the surrounded environment contains:

1. Consequence: An estimation of the amount of pollutant in the level of the guidelines (TPH/PAHs);
2. Impact intensity/severity (the results of the ecological risk assessment /guideline were determined as the impact intensity);
3. Impact probability/ frequency;
4. And considering the predetermined (current) control actions.

Therefore, each of them can be defined as follows:

- 1- Consequence: Concentration of contaminant (TPH/PAHs) in the effluents of each petrochemical company was compared with the guidelines and for TPH it was defined in four levels according to guidelines (5 – 10 mg/l). (U.S.EPA, 1995; US EPA New England, 2010; UWI, 2004):

- I- Insignificant : (Unpolluted)  $1 < \text{TPH} \leq 5$ ;
- II- Minor: (Low)  $5 < \text{TPH} \leq 10$ ;
- III- Moderate: (Moderate)  $10 < \text{TPH} \leq 20$ ;
- IV- Major: (High)  $\text{TPH} \geq 20$ .

For PAHs it was defined in two levels:

- I- Insignificant: (Unpolluted)  $\Sigma \text{PAHs group I and II} < \text{guideline value}$   
( $< 10000$  and  $< 100000$  respectively).

- II- Significant: (Polluted) ΣPAHs group I and II > guideline value (>10000 and >100000 respectively).

2- Impact intensity (severity): this matrix is organised into 4 levels due to the result of ERA (Ecological Risk Assessment- the terminology based on ecological risk (PAH)):

- I- Low ecological risk  $RI < 50$ ;
- II- Moderate ecological risk  $50 \leq RI < 100$ ;
- III- High ecological risk  $100 \leq RI < 200$ ;
- IV- Very high ecological risk  $RI > 200$ .

Also, this terminology based on TPH concentration is:

- I- Unpolluted area (No Environmental damage) – 10-15 µg/g;
- II- Slightly polluted area (Short term Environmental damage)- 15-50 µg/g;
- III- Moderately polluted area (Moderate environmental damage)- 50-200 µg/g;
- IV- Extensive Environmental damage: (Heavily polluted area)- > 200µg/g;

3- Impact probability<sup>1</sup>:

- I- Unlikely: sometimes in a month (Could happen, but rarely);
- II- Possible: sometimes in a week (Might happen at some time);
- III- Likely: sometimes in a day (Probably will occur in most circumstances);
- IV- Almost certain: discharge continuously (Expected to occur in most

circumstances).

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<sup>1</sup> Rare: sudden or emergency discharges (has never occurred before)

4- Control indices (mitigating index) this matrix is also organised into 3 levels as follows:

- I- Its treatment technique is adequate ( $1 < \text{TPH} \leq 5$ );
- II- Its treatment technique is not completely adequate ( $5 < \text{TPH} \leq 10$ );
- III- Its treatment technique is not adequate/there is not any treatment ( $\text{TPH} > 10$ ).

In general, the final equation was:

Environmental Impact = Consequence x Probability x Intensity x Control Indices.

Thus, due to the defined levels, the result of this terminology is Risk Priority Number and it can be categorized as follows for TPH ( $\text{RPN}_{\text{TPH}} = 4 \times 4 \times 4 \times 3 = 192$ ) and the environmental aspects are categorized as follows:

- 1-  $\text{RPN}_{\text{TPH}} \geq 192$ : is considered as significant environmental aspects (should mitigate the risk and It requires immediate executive management attention, control action must be immediately implemented);
- 2-  $100 < \text{RPN}_{\text{TPH}} \leq 191$ : is considered as an important environmental aspects (should mitigate the risk and control action must be implemented);
- 3-  $50 < \text{RPN}_{\text{TPH}} \leq 99$ : is considered as moderate environmental aspects (should mitigate the risk in long term;
- 4-  $0 < \text{RPN}_{\text{TPH}} \leq 49$ : is considered as low environmental aspects (it does not need control actions but it should be monitored).

Also PAHs RPN is:

$$\text{RPN}_{\text{PAHs}} = 2 \times 4 \times 4 \times 3 = 96$$

Thus the environmental aspects are categorized as follows:

- 1-  $RPN_{PAHs} \geq 96$ : is considered as significant environmental aspects (should mitigate the risk and It requires immediate executive management attention, control action must be immediately implemented);
- 2-  $48 < RPN_{PAHs} \leq 95$ : is considered as an important environmental aspects(should mitigate the risk and control action must be implemented);
- 3-  $24 < RPN_{PAHs} \leq 47$ : is considered as moderate environmental aspects (should mitigate the risk in long term;
- 4-  $0 < RPN_{PAHs} \leq 23$ : is considered as low environmental aspects (it does not need control actions but it should be monitored).

### **3.5. Statistical Analysis**

In this research, statistical analyses (researching the facts by use of mathematical methods) were performed using Microsoft Excel and SPSS 17 software (SPSS,Chicago, IL) to estimate statistical tests on monitoring and bioassays data.

Variations of spatial and temporal data was analyzed by Box-Whisker plots which show the minimum and maximum concentration (with the mean value), correlation coefficient (to understand the interaction among variables) and also multivariate techniques such as cluster analysis (CA) and principal components analysis (PCA). The cluster analysis was used to classify a set of data into different groups based on similarity. This method has been widely applied to environmental assessment to classify the data into temporal and spatial scales. The principal components analysis is known as dimensional

reduction because this method is able to decrease the dimensionality of the primary set of data and to compress data into a lower dimensional matrix (Kitsiou & Karydis, 2011).

Therefore, one dimensional statistical analysis (descriptive statistic, ANOVA, person correlation) and multi-dimensional statistical analysis (CA- cluster analysis and PCA - Principal Component Analysis) were applied to calculate and classify the data.

## CHAPTER IV: RESULTS AND INTERPRETATIONS

In this study , the distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in sediment as well as total petroleum hydrocarbon (TPH) have been investigated in areas of anthropogenic pollution in the Musa Bay (Northwest of the Persian Gulf). Also, some biological analyses were performed to assess the ecological status of benthic communities. During this investigation, the wastewaters of PETZONE were monitored too. The results of the study are as follows.

### 4.1.Sediment Quality Assessment

#### 4.1.1. Total Petroleum Hydrocarbons

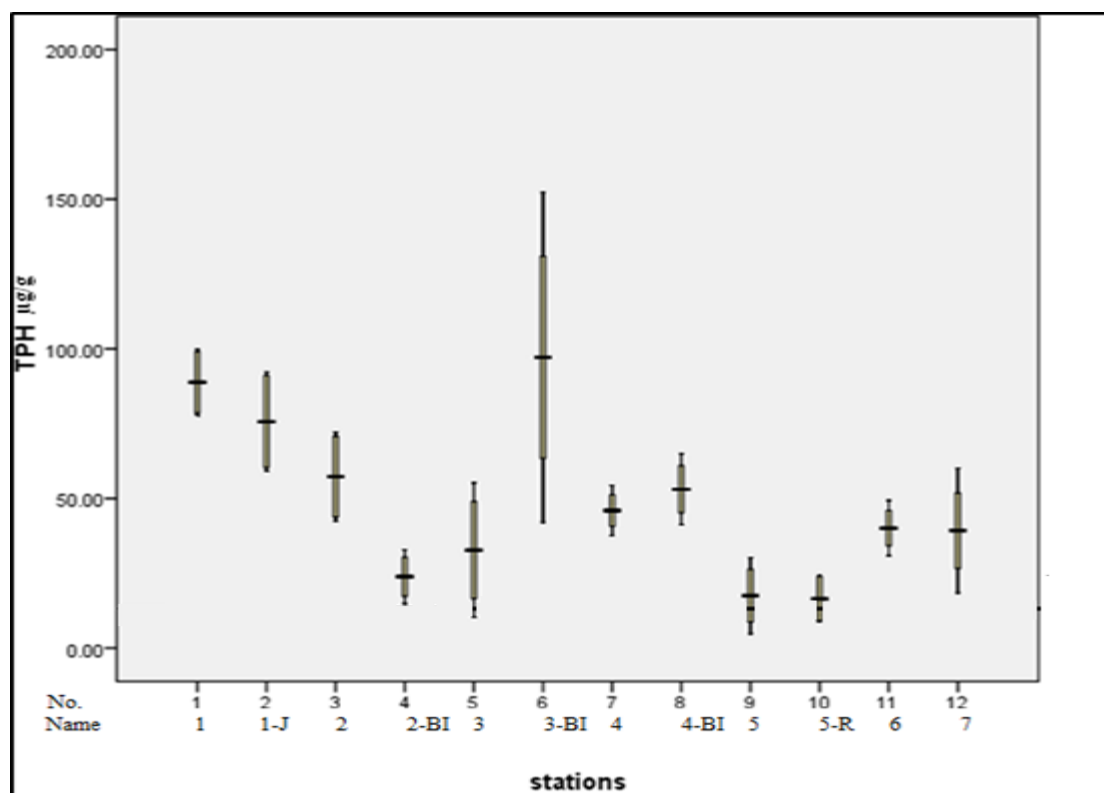
The average concentrations of TPH obtained in the present investigation are shown in Table 4.1. The TPH concentration of sediment samples presented an average value of 48.98 µg/ g and ranged from 16.48 to 97.15 µg/ g dry weight and the highest TPH level was observed at 3-BI (97.15 µg/g). The TPH concentrations of the stations can be arranged as follows: 3-BI>1>1-J>2>4-BI>4>6>7>3>2-BI>5>5-R

**Table 4.1.** The average concentration of TPH in the sampling stations

Musa Bay				TPH µg/g
No.	Station code	Mean	Std. Deviation	Guideline
1	1	88.81	11.85	Moderately polluted
2	1-J	75.65	17.80	Moderately polluted
3	2	57.32	15.65	Moderately polluted
4	2-BI	43.84	8.04	Slightly polluted
5	3	32.73	20.06	Slightly polluted
6	3-BI	97.15	46.08	Moderately polluted
7	4	45.93	7.07	Slightly polluted
8	4-BI	53.04	10.18	Moderately polluted
9	5	17.51	11.08	Slightly polluted
10	5-R	16.48	8.51	Slightly polluted
11	6	40.05	7.81	Slightly polluted
12	7	39.25	17.33	Slightly polluted
-	Total	48.98	30.36	Slightly polluted

Slightly polluted  
Moderately polluted


Concentration of TPH in each sampling station was compared with the guideline value and at all of the stations, the concentration of TPH was greater than the natural background value (unpolluted area /natural background level: 10-15  $\mu\text{g/g}$  (Massoud, et al., 1996)).



**Fig.4.1.** Average concentration of TPH ( $\mu\text{g/g}$ ) in Musa Bay sediment and the Box-Whisker Plots

As shown in Figure 4.1, high concentration of TPH was observed at the first three stations near the main PETZONE outlets and also near the most important outlet of Bandar-e- Imam Khomeini petrochemical company. The concentration of TPH reached a peak at station (3-BI- maximum value: 97.15  $\mu\text{g/g}$ ). As it was mentioned before, the concentration of TPH reached a maximum value at station 3-BI, while station 5 and 5-R (No.9 and 10: 17.51  $\mu\text{g/g}$  and 16.48  $\mu\text{g/g}$ , respectively) presented the lowest concentration.



Lastly, the amount of TPH increased gradually at stations 6 and 7. The TPH concentration reached a maximum in the east, near the main outlets of the PETZONE and Imam Khomeini petrochemical company east and southeast outlets. The mangrove lines are located in the east part and close to the main outlets of the PETZONE (outlets of Jafari and Zangi Creeks). During low tide, Jafari and Zangi Creeks which are located inside the PETZONE, interchange their water with Musa Bay (Fig. 4.2).



**Fig.4.2.** Location of the connective canals of Jafari and Zangi Creeks (Google- Earth 6.1.0.5001, 2011- 1780 m )

In 2000, the Mangrove Afforestation Program was initiated in the coastal area surrounding the aforementioned creeks and Musa Bay, including PETZONE and the region surrounding Mahshahr oil export terminal to increase the amount of green space around industrial zones<sup>1</sup>. This program was performed in this area according to the characteristics of these types of forests; so, as the hydrodynamic energy time decreases in these areas, these types of forests can trap suspended solids; thus, enough time is available for the storage and re-deposition of fine particles. Due to the high total organic carbon content, aerobic conditions and rapid change of burial, the potential for the deposition of anthropogenic pollutants adsorbed by sediments in mangrove forests is high (Furukawa, Wolanski, & Mueller, 1997; Cunha-Lignon et al., 2009).

Stations 5 and 5-R are located near the port of Razi and the outlet of Razi petrochemical company and the concentration of TPH were close to the natural background value (10-15 µg/g- (Massoud, et al., 1996; De mora et al, 2010b)) at these station. Station 6 is located near the Bandar-e-Imam Khomeini port, and station 7 is situated in the mouth of Marimus Creek. However, effluent outlets were not present alongside these stations. As a result, this stations were classified as slightly polluted (slightly polluted area /upper permissible limits:15-50 µg/g (Massoud, et al., 1996)).

On the other hand, due to another guideline, TPH concentrations more than 500 µg/g are indicative of significant pollution and less than 10 µg/g are considered as unpolluted sediments (Volkman, Holdsworth, Neill & Bavor, 1992).

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<sup>1</sup> <http://www.bipc.org>

Finally, the sediment quality guidelines (SQGs) that are applied to assess adverse biological effect (Khairy et al., 2009; Ralf Hubner et al., 2009). The TEL value has been estimated as the concentration of contaminants with a relatively low effect on biological communities (in this study is natural background value of 10-15 µg/g), and PEL is a concentration of contaminants with high toxic effects (500 µg/g can be considered as significant pollution) ( Long & Morgan, 1990; Volkman, Holdsworth, Neill & Bavor, 1992; Long, MacDonald, Smith & Calder, 1995; Hübner et al., 2009).


The overall toxicity of TPH was estimated by PEL quotients (PELq's) as it shown in Table 4.2.

**Table 4.2.** The value of PELq in each sampling station based on the concentration of TPH in Musa Bay

station	Mean value µg/g	PELq values*
1	88.81	0.17
1-J	75.65	0.15
2	57.32	0.11
2-BI	43.84	0.08
3	32.73	0.06
3-BI	97.15	0.19
4	45.93	0.09
4-BI	53.04	0.10
5	17.51	0.03
5-R	16.48	0.03
6	40.05	0.08
7	39.25	0.07
Total	48.98	0.10**

\* Based on SQG (Volkman, Holdsworth, Neill & Bavor, 1992 ; De mora et al, 2010b)

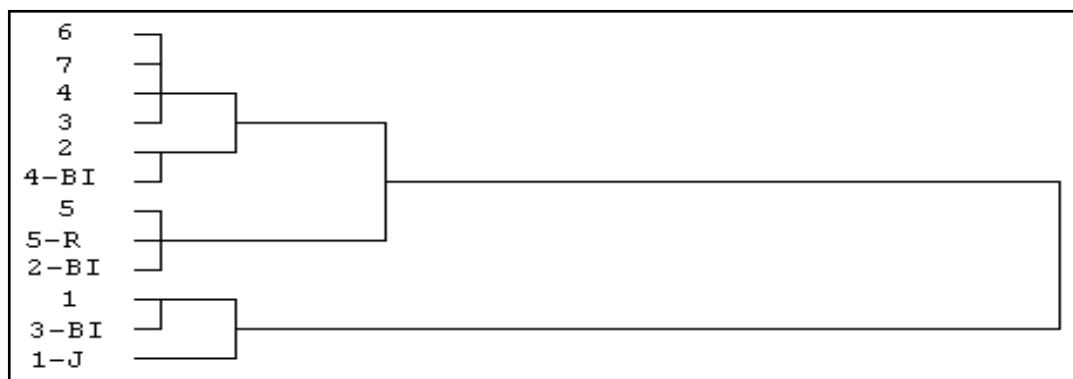
\*\* Calculated with rounded values 0.10 (0.9897)

(0.1<PELq<0.5) 

The range of slightly toxic effects (0.1<PELq<0.5) was detected for most of the stations which are located in the vicinity of the Bandar-e-Imam Khomeini and PETZONE

effluent outlets. Also, the rest of the stations can be categorized in the range of non-toxic ( $PELq < 0.1$ ). In general, the average concentration of TPH and related  $PELq$  ( $49.98 \mu\text{g/g}$  and  $0.01$ , respectively) classified this area in the range of slightly toxic effects ( $0.1 < PELq < 0.5$ ).

Moreover, the average cluster analysis results for TPH showed that this factor can be classified into four groups as follows: Group I: 6, 7, 4, 3; group II: 2, 4-BI; group III: 5, 5-R, 2-BI and group IV: 1, 3-BI, 1-J. In addition, high concentrations of TPH were observed at group IV (Figure 4.3).



**Fig4.3.** A dendrogram representation of a hierarchical cluster analysis of TPH in the Bay

Thus, according to the cluster analysis and the guideline, most of the stations which are located in the east part of the study area are categorized in moderate level (or close to the lowest level of the moderate level).

Moreover, the results of ANOVA analysis showed that, there was not any significant difference between the concentrations of TPH and stations ( $p > 0.05$ ,  $df 16$ ) and also sampling times ( $p > 0.05$ ,  $df 4$ ).

#### 4.1.2. Polycyclic Aromatic Hydrocarbons


Concentrations of PAHs in sediment samples obtained in the present investigation are shown in Table 4.3.

**Table 4.3.** PAHs concentrations in the sampling sediments of Musa Bay (ng/g, dry wt.)

Station No.	1	2	3	4	5	6	TEL	PEL	ER-L	ER-M
Station name	1	1-J	2	2-BI	3	3-BI				
PAHs										
Na	12.56	5.28	20.50	23.38	24.83	217.83	34.6	391	160	2100
Acpy	57.42	51.90	89.64	55.15	130.56	113.64	5.87	128	44	640
Acp	3.27	2.38	17.05	ND	34.74	47.96	6.71	88.9	16	500
Flu	26.33	18.78	104.13	26.30	138.89	150.44	21.2	144	19	540
Phen	153.36	100.76	520.50	97.07	1003.68	582.74	86.7	544	240	1500
Ant	76.55	54.96	131.28	94.85	237.47	196.94	46.9	245	853	1100
Flur	77.06	47.22	113.90	83.32	228.59	127.92	113	1494	600	5100
Py	92.32	63.55	151.26	76.53	317.94	183.63	153	1398	665	26000
BaA	72.87	56.23	62.49	36.43	246.84	106.53	74.8	693	261	16000
Chr	53.8	41.83	73.14	42.68	235.24	105.99	108	846	384	2800
BbF	ND*	1.04	ND	ND	48.78	12.39	-	-	320	1880
BkF	5.11	2.54	2.14	ND	34.16	11.51	-	-	280	1620
BaP	6.27	7.83	5.38	2.14	25.22	13.42	88.8	763	430	1600
IP	3.91	ND	20.93	ND	ND	2.66	-	-	-	-
DbahA	ND	ND	ND	ND	ND	ND	6.22	135	63.4	260
BghiP	5.54	ND	ND	ND	6.32	1.51	-	-	430	1600
Σ PAHs	646.37	454.3	1312.38	537.89	2713.33	1875.17	1684	16770	4022	44792
Station No.	7	8	9	10	11	12	TEL	PEL	ER-L	ER-M
Station name	4	4-BI	5	5-R	6	7				
PAHs										
Na	32.31	39.31	19.53	17.15	14.62	ND	34.6	391	160	2100
Acpy	109.73	96.42	67.37	77.94	25.06	11.86	5.87	128	44	640
Acp	68.82	26.06	4.15	ND	10.09	ND	6.71	88.9	16	500
Flu	580.34	94.49	51.57	62.78	8.22	27.59	21.2	144	19	540
Phen	2820.60	598.78	220.83	203.21	95.24	27.48	86.7	544	240	1500
Ant	668.39	165.55	121.25	216.83	50.25	35.56	46.9	245	853	1100
Flur	2700.61	216.09	133.68	146.13	220.42	30.14	113	1494	600	5100
Py	1772.81	230.48	158.33	162.38	58.44	38.58	153	1398	665	26000
BaA	7079.15	308.84	181.15	184.94	46.23	15.69	74.8	693	261	16000
Chr	5510.74	242.98	148.22	202.95	34.89	11.93	108	846	384	2800
BbF	2898.68	54.08	91.36	330.42	6.30	ND	-	-	320	1880
BkF	1327.78	45.64	50.49	170.43	5.83	1.97	-	-	280	1620
BaP	911.57	41.64	43.88	111.41	8.318	5.82	88.8	763	430	1600
IP	83.42	ND	61.35	153.30	21.75	6.78	-	-	-	-
DbahA	ND	ND	20.77	20.91	ND	ND	6.22	135	63.4	260
BghiP	94.05	ND	36.46	77.23	7.39	3.13	-	-	430	1600
Σ PAHs	26659.06	2160.42	1410.46	2138.09	613.12	216.56	1684	16770	4022	44792

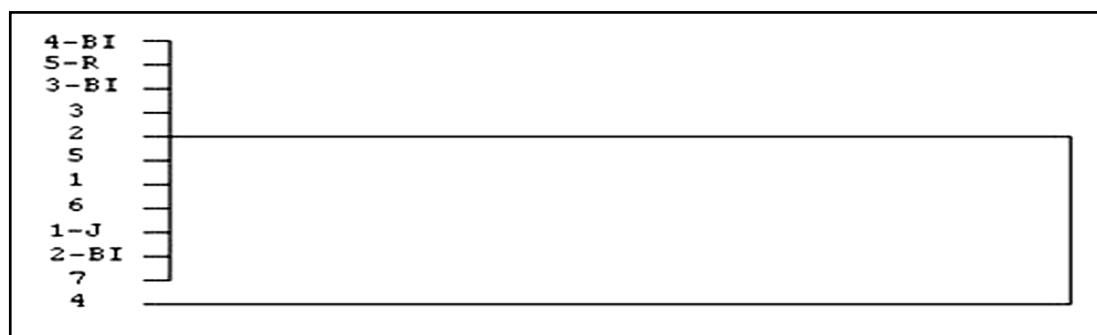
\* ND: Not Detected

TEL: Threshold Effects Level; PEL: Probable Effects Level; ERL: Effect Range Low; ERM: Effect Range Median (NOAA, 1999; Long et al., 1995; Long, Ingersoll & MacDonald, 2006)

More than ERL= 4022 ng/g dry weight 

Most values were exceptionally low, except for the sediments near the station 4, which is located near the aromatic outlet of Imam Khomeini petrochemical company (station 4: BI-PC Aromatic effluent outlet) in which its concentration level was more than the NOAA sediment quality guideline value (ERL= 4022 ng/g dry weight) (Long et al., 1995).

The cluster analysis of total PAH showed that this factor can be classified into two groups and classified station 4 significantly different from other stations (Figure.4.4).



**Fig.4.4.** A dendrogram representation of a hierarchical cluster analysis of the PAHs in the Bay



PAHs in sampling sediments from the Musa Bay ranged from 216.57 (216.566931) to 26,659.07 ng/g dry weight with a mean value of 3394.76 ng/g (3.40  $\mu\text{g/g}$ ). In addition, the average and maximum concentration of PAH compositions in the area were compared to the guidelines (Table4.3) (Long et al., 1995; Li et al., 2006).

Furthermore, the results of the ANOVA statistical analysis did not show any significant difference between the concentration of PAHs and stations, and also during the sampling period ( $p > 0.05$ ).

**Table4.4.** Average and maximum concentration of PAHs (ng/g dry weight) in the area compared to the guidelines

PAHs compounds	Musa bay		Guideline			
	Ave	Max	ER-L	ER-M	TEL	PEL
Na	35.61	217.83	160	2100	34.6	391
Acpy	73.89	130.57	44	640	5.87	128
Acp	17.87	68.82	16	500	6.71	88.9
Flu	107.49	580.35	19	540	21.2	144
Phen	535.36	2820.60	240	1500	86.7	544
Ant	170.83	668.40	85.3	1100	46.9	245
Flur	343.76	2700.62	600	5100	113	1494
Py	275.52	1772.81	665	2600	153	1398
BaA	699.79	7079.16	261	1600	74.8	693
Chr	558.70	5510.74	384	2800	108	846
BbF	286.92	2898.68	Na	Na	-	-
BkF	138.14	1327.79	Na	Na	-	-
BaP	98.57	911.57	430	1600	88.8	763
IND	29.51	153.31	Na	Na	-	-
DbahA	3.47	21	63.4	260	6.22	135
BghiP	19.31	94	NA	NA	-	-

ERL: Effect Range Low; ERM: Effect Range Median; Ave: Average; Max: Maximum (NOAA, 1999; Long et al., 1995; Long et al., 2006)

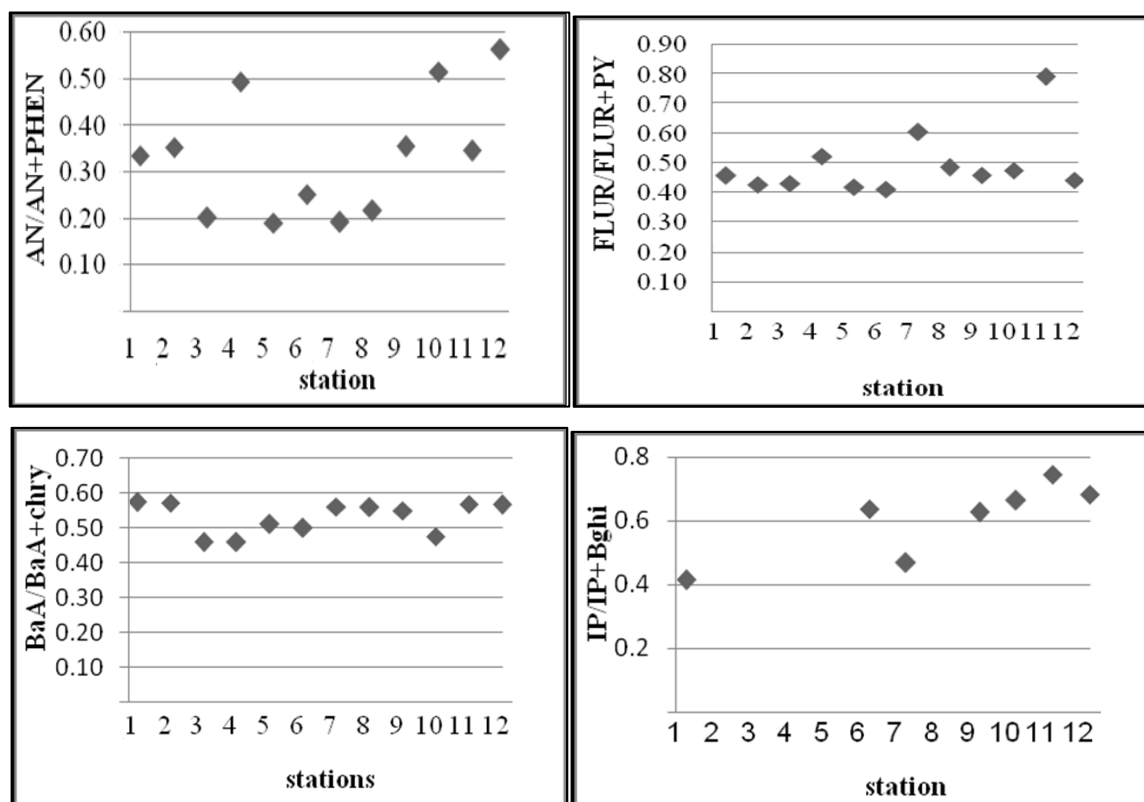
More than ERL   
 More than TEL 

According to the table 4.4, average concentrations of PAH components in the sediments of the Musa Bay were more than the guideline values (except Dibenzo(a,h)anthracene (DbahA)).

#### 4.1.3. Source Identification of Polycyclic Aromatic Hydrocarbons

Some high-molecular-weight PAHs such as BaA, Chy, BbF, BkF, BaP, InP and DibA are known as toxic PAHs because of their mutagenic and carcinogenic effects on humans and other organisms (Hale et al., 2012; Khairy, et al., 2009). Pyrogenic and petrogenic sources are typically distinguished based on the ratios of individual PAHs, which are identified based on molecular mass. PAHs of molecular mass 178 and 202 are commonly used to recognize between combustion and petroleum sources of PAHs.

According to the PAH isomer ratios (Yunker et al., 2002; Li et al., 2006; Wang et al., 2011; Semlali et al., 2012;), the following isomer ratios have been used to identify potential sources of PAHs: Ant/ An+Phe, BaA/BaA + Chry, Flu/Flu + Pyr and IP/IP + Bghi and the results are shown in Fig.4.5.



**Fig.4.5.**PAH pair ratios for the identification of sources

The isomer pair ratios of PAHs were calculated. The Ant/Ant + Phe ratio showed that the main source of PAHs was combustion (Ant/(Ant + Phe) > 0.1 were typical of combustion source). In contrast, the Flu/Flu + Pyr ratio showed that in the most of the sampling stations, the main source of pollution was combustion of petroleum (0.5 > Flu/(Flu + Pyr) > 0.4), except for stations 2-BI, 4 and 6, which received PAHs from different sources, (Flu/(Flu + Pyr) > 0.5) including were mainly from combustion of grass, wood and



coal. The BaA/BaA + Chry ratio showed that the main source of PAHs at all of the sampling stations was combustion ( $\text{BaA}/(\text{Chry} + \text{BaA}) > 0.35$ ).

Finally, the ratio of IP/IP+BP, at about half of the sampling stations were shown that the main source of PAHs was petroleum origin and also from oil combustion ( $\text{IP}/\text{IP}+\text{BP} < 0.2$ : from petroleum origin input; PAHs with  $0.2 < \text{IP}/\text{IP}+\text{BP} < 0.5$ : mainly from oil combustion), while the rest of them were greater than 0.5, indicating that the input of PAHs were mainly from coal, wood and grass combustion.

Rotated component loadings of the three principal components of PAHs in Musa Bay sediments indicated that (Table 4.5):

PC1 could explain 70.83% of the total variance in the data. This factor strongly affected the concentration of Flu, Ant, Flur, Py, BaA, Chr, BbF, BkF, BaP, Phen, Acp, and BghiP; thus, the main sources of contamination were incomplete combustion and fuel pyrolysis (Liu et al., 2008; Falahudin, Munawir, Arifin & Wagey, 2012).

PC2 was responsible for 15.60% of the total variance in the data and had a significant impact on the BaP and IP concentration. Thus, the main sources of contamination were incomplete combustion and fuel pyrolysis. The third PC, which is responsible for 9.42% of the variance, was not associated with any of the PAHs; thus it is related to an unknown source.

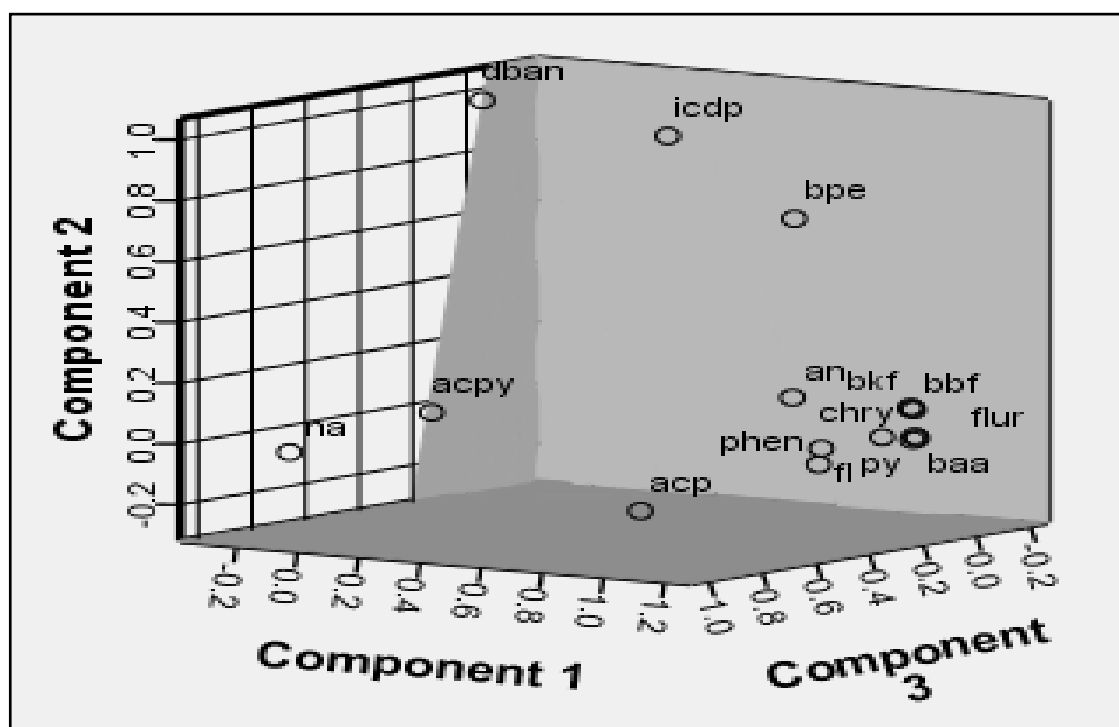
**Table4.5.** Rotated component loadings of the three principal components of PAHs in Musa Bay sediments

PAHs compounds	PC1	PC2	PC3
Na	0.08	-0.55	0.67
Acpy	0.49	-0.37	0.64
Acp	0.80	-0.51	0.26
Flu	0.98	-0.15	0.02
Phen	0.96	-0.19	0.00
Ant	0.98	-0.02	0.14
Flur	0.98	-0.00	-0.17
Py	0.99	-0.04	-0.09
BaA	0.98	0.00	-0.18
Chr	0.98	0.00	-0.17
BbF	0.98	0.08	-0.14
BkF	0.98	0.09	-0.13
BaP	0.98	0.08	-0.13
IP	0.44	0.80	0.34
DbahA	-0.04	0.83	0.49
BghiP	0.77	0.60	0.17
Variance %	70.83	15.60	9.42
Cumulative %	70.83	86.44	95.86

Greater than 0.7



Naphthalene (Na), Acenaphthylene (Acpy) , Acenaphthene(Acp), Fluorene (Flur), Phenanthrene (Phen), Anthracene (Ant), Fluoranthene (Flu) , Pyrene (Py), Benzo(a)anthracene (BaA) , Chrysene (Chr), Benzo(b)fluoranthene(BbF), Benzo(k) fluoranthene (BkF) , Benzo (a) pyrene (BaP), Dibenzo(a,h)anthracene (DbahA) , Benzo (g,h,i) perylene (BghiP) , Indeno (1,2,3-cd) pyrene (IP)



**Fig.4.6.** Component Plot in rotated space - three principal components of PAHs in Musa Bay sediments

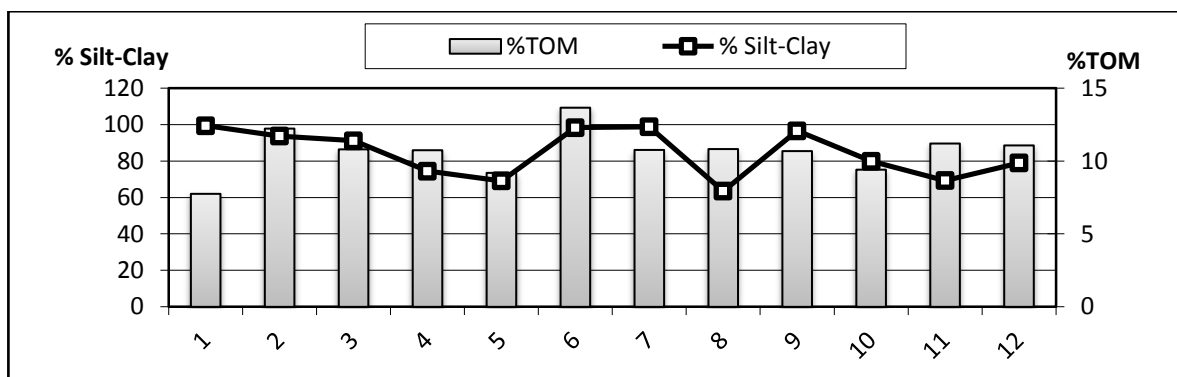
The L/H-PAH ratio is accepted as a practical method for assessing weathering based on the differences between the low molecular weight and high molecular weight of PAH compounds (Liu et al., 2009). These results demonstrated that the concentrations of high-molecular-weight PAHs were greater than that of low-molecular-weight PAHs in most stations which can be related to high resistance of these types of compounds to microbial degradation (Rocher, Garnaud, Moilleron, & Chebbo, 2004).

#### 4.1.4. Analysis of Surface Sediment Components

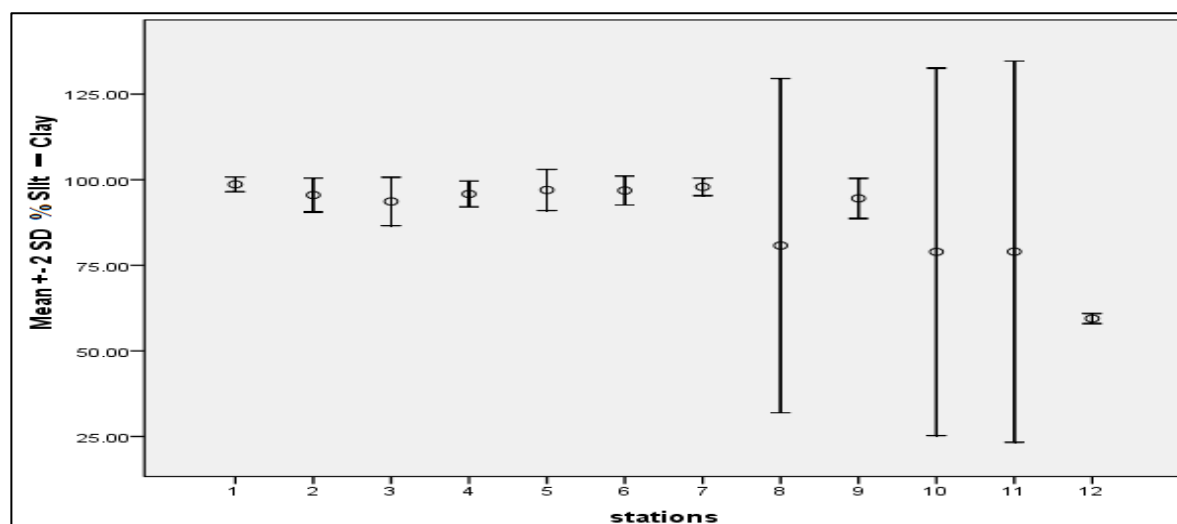
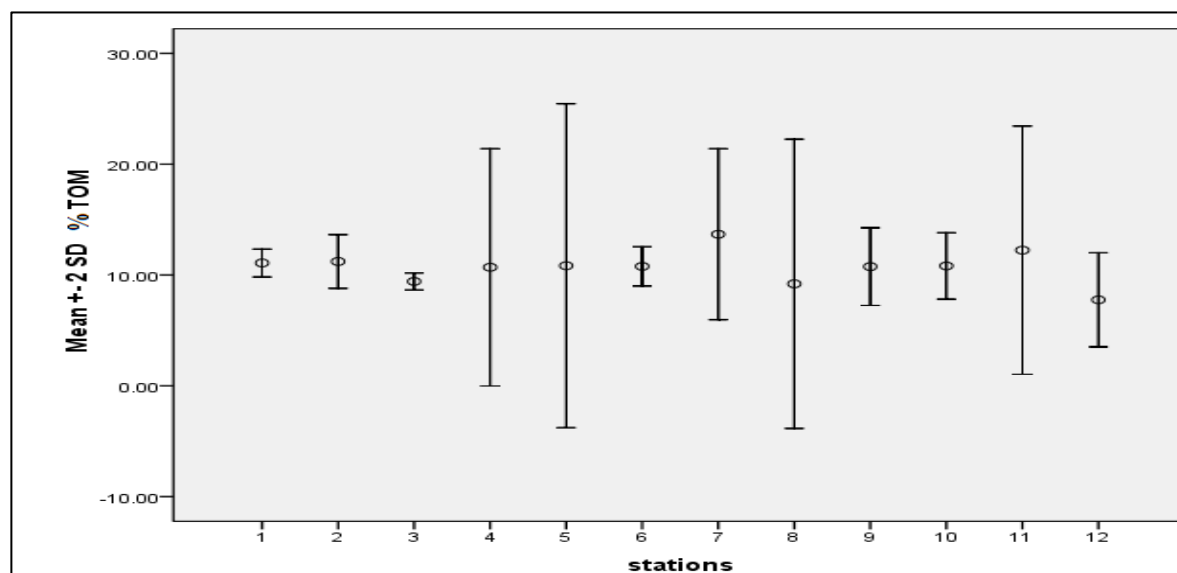
Marine soft analysis of the sediment grain size of the Musa Bay demonstrated that, fine-grained sediment was predominant at almost all stations except the station 7 (N0.12), and varied between 58.94% - 99.40% with an average 89.01% silt-clay (highest percentage of silt-clay was observed at station 4 (No.7)). Owing to the greater concentration of organic matter in fine-sized sediments than coarse-sized (Meyers, Leenheer, Eaoie, & Maule, 1984; Hedges & Keil, 1995), the percentage of TOM in the sampling stations was monitored in sediment samples too. Its concentration varied between 4.59% - 16.40 % with an average 10.70% silt-clay (Table 4.6 and Fig.4.7).

**Table 4.6.** The average percentage of TOM and Silt-Clay in the Musa Bay sediments

	Station	1	1-J	2	2-BI	3	3-BI	4	4-BI	5	5-R	6	7	Total
%TOM	Mean	11.08	11.21	9.42	10.69	10.83	10.77	13.67	9.20	10.75	10.81	12.24	7.76	10.70
	SD	0.62	1.21	0.38	5.35	7.30	0.88	3.85	6.52	1.75	1.49	5.60	2.12	3.17
% Silt-Clay	Mean	98.64	95.51	93.65	95.84	97.00	96.85	97.91	80.76	94.55	78.93	78.99	59.46	89.01
	SD	1.074	2.48	3.53	1.88	3.00	2.11	1.27	24.40	2.93	26.83	27.82	0.73	15.18



A.



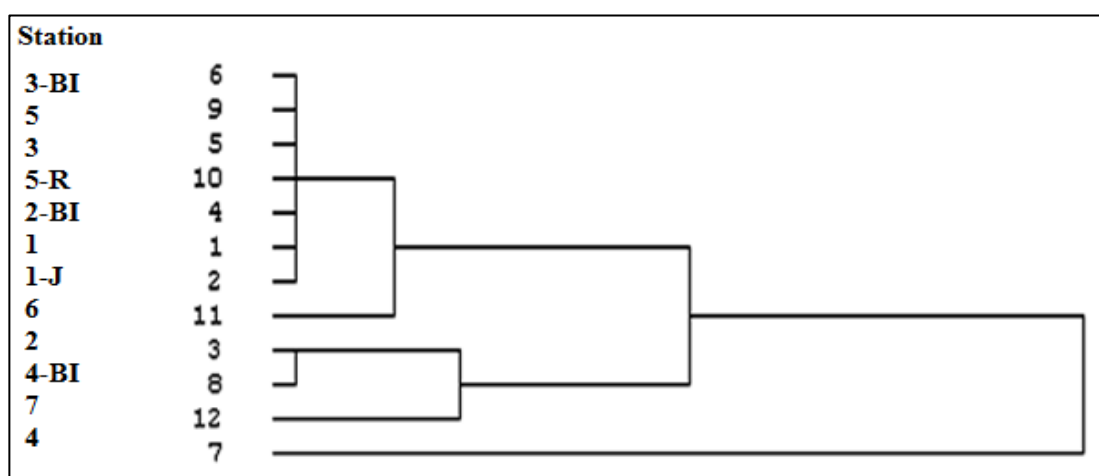
B.

**Fig.4.7. A.** Variation of %TOM and %Silt clay in Musa Bay sediments  
**B.** Mean value of %TOM and %Silt-Clay in sampling stations during four times sampling

In addition, Two-Way ANOVA analysis showed significant difference between the concentration of organic matter and sampling times ( $p < 0.05$ ,  $f = 18.38$ ,  $df = 1$ ); while, two way ANOVA analysis of %silt and clay was not shown any significant difference in sampling stations and time.

Moreover, the cluster analysis of TOM (Total organic Matter) in the sampling stations of Musa bay showed three significant groups and clustered stations 3-BI, 5, 3, 5-R, 2-BI, 1 and 1-J in same category. Thus, more than half of the stations are classified in the first group with the high concentration of TOM which are located in the vicinity of main effluent outlets of the PETZONE, Razi and Bandar-e-Imam Khomeini petrochemical companies..

The highest concentration of organic matter was observed at station 3-BI (No.6), then the cluster showed that stations 6, 4-BI and 2 (No. 11, 8 and 3 respectively) had the lower concentration than station 4 and the rest had lowest concentration of organic matter than other groups.

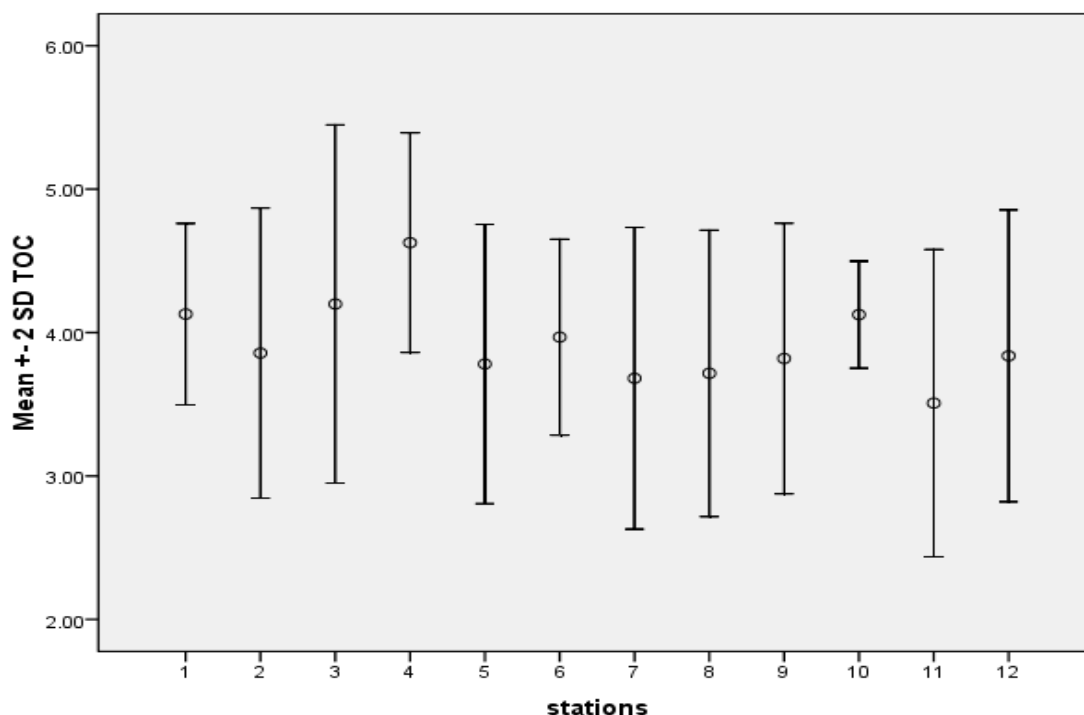


**Fig.4.8.** A dendrogram representation of a hierarchical cluster analysis of the average % TOM in Musa Bay sediments

The other parameter which was measured in the study area was total organic carbon (TOC) with the mean value of 3.94% and varied between 2.71% - 4.93% (Table 4.7).

**Table 4.7.** The average percentage of TOC in the Musa Bay sediments

TOC%	Station	1	1-J	2	2-BI	3	3-BI	4	4-BI	5	5-R	6	7	Total
	Mean	4.12	3.85	4.19	4.62	3.78	3.96	3.98	3.71	3.81	4.12	3.50	3.83	3.93
	SD	0.31	0.50	0.62	0.38	0.48	0.34	0.52	0.49	0.47	0.18	0.53	0.50	0.49



**Fig.4.9.** Mean value of %TOC in sampling stations during four times sampling

The concentration of TOM and TOC are exceed the EPA guideline value (more than 1%) (US.EPA,2001), in this area. Moreover, high concentrations of TOC were observed at stations 1, 3, 4 and 10 which are located near the connective canals of Jafari and Zangi creeks (junction of these creeks in Musa Bay), effluent outlets of Bandar-e- imam Khomeini and Razi petrochemical companies. The rest of the stations were lower than 4% (%TOC < % 4).

#### **4.1.5. PAH Benchmark Calculation for Sediment**

According to US. EPA (2010a) definition, “benchmark is a chemical concentration in water or sediment, above which there is the possibility of harm or risk to the humans or animals in the environment”. The acute toxicity (adverse effects resulting from a substance in a short term) and chronic toxicity (adverse effects resulting from a substance in a long term) of substances were determined by U.S.EPA to calculate benchmarks.

In this study, the approach was based on the procedures described in US. EPA PAH ESB 2010. The potency divisors (Acute and Chronic Potency Divisor) were used in the calculations, which are indicated that the amount of individual chemical (such as pyrene, phenantherene and etc.), by itself can cause an adverse effect. PAHs bind to organic carbon when they are present in sediments; thus, it can decrease their bioavailability and toxicity (U.S.EPA, 2010a). Therefore, the concentration of total organic carbon is the other factor which was measured in this study and PAHs benchmark was calculated for all 16PAHs in each sampling station.

In order to calculate the differences in bioavailability of PAHs in the sampling sediments, the concentrations of PAH components (dry weight) in each station are divided by the organic carbon concentration due to US EPA procedure (Table 4.7) (U.S.EPA, 2010b).

Thus, PAH benchmark calculation for sediment samples was performed based on following steps:

- 1- Normalize the concentrations of PAHs by dividing by the fraction organic carbon;

2- Divide organic carbon-normalized values by their "potency divisors" (from the sediment benchmark table Appendix III);

3- Add the individual fractional contributions of each PAH compound together (Table 4.8).

**Table 4.8.** Benchmark calculation of the sampling sediments

No.	Station	TOC%	Acute Potency Ratio ( $\mu\text{g/kg}$ Organic Carbon) (For all 16 PAHs)	Chronic Potency Ratio ( $\mu\text{g/kg}$ Organic Carbon) (For all 16 PAHs)
1	1	4.12	0.043	0.0177
2	1-J	3.85	0.024	0.100
3	2	4.19	0.093	0.387
4	2-BI	4.62	0.054	0.222
5	3	3.78	0.156	0.650
6	3-BI	3.96	0.485	2.017
7	4	3.68	0.706	2.936
8	4-BI	3.71	0.151	0.626
9	5	3.81	0.071	0.295
10	5-R	4.12	0.073	0.305
11	6	3.50	0.044	0.184
12	7	3.83	0.009	0.036

Greater than 1



As it shown in Table 4.8, in this study, the sum of Chronic Potency Ratio showed that, the chronic benchmark was not more than the guideline at all the stations (it is exceeded when the sum exceeds 1.0) except stations 3-BI and 4 which are located near the effluent outlets of Bandar-e- imam Khomeini petrochemical company (south east and Aromatic outlets of aforementioned petrochemical company).



#### 4.1.6. Biological assessment

##### 4.1.6.1. Spatial and Temporal Distribution of Benthic Communities

The results of the analysis of the spatial and temporal distributions of benthic composition are summarized in Table 4.9 and Table 4.10.

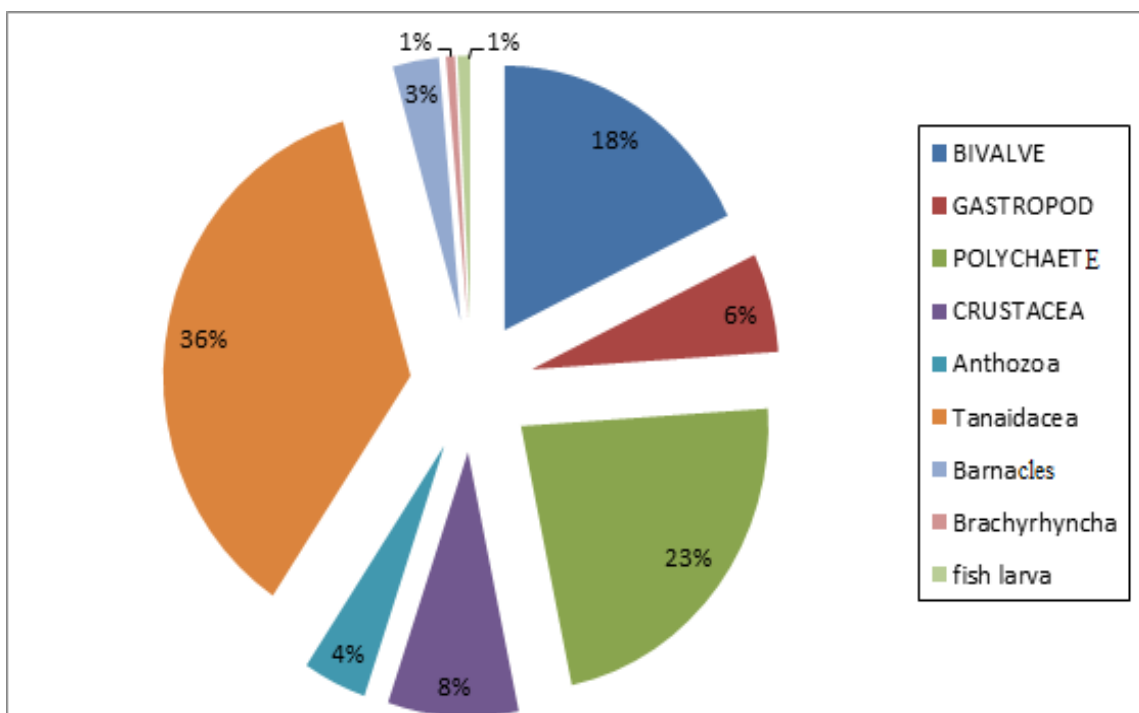
**Table 4.9.** Total abundance (ind/m<sup>2</sup>) of macrofaunal taxa in different stations over different time intervals

St.		Bivalve	Gastropod	Polychaete	Crustacea	Anthozoa	Tanaidacea	Barnacles	Brachyrrhyncha	Fish Larve
1	Mean	168.67	83.00	88.00	308.00	-	-	-	-	-
	SD	189.68	38.18	0.00	.-	-	-	-	-	-
2	Mean	146.25	110.00	88.00	-	-	-	11.00	5.00	10.67
	SD	91.75	31.11	.-	-	-	-	.	-	5.86
3	Mean	118.33	31.00	328.00	-	-	-	-	-	17.00
	SD	40.25	1.41	-	-	-	-	-	-	2.83
4	Mean	446.00	32.00	231.00	95.50	-	5840.00	-	-	3.00
	SD	381.84	-	91.92	51.62	-	.	-	-	.
5	Mean	203.00	32.00	299.00	44.00	-	3366.00	-	-	-
	SD	117.58	.	52.33	-	-	-	-	-	-
6	Mean	148.33	76.00	883.00	-	-	-	-	-	-
	SD	87.75	16.97	1059.25	-	-	-	-	-	-
7	Mean	90.00	-	230.00	-	-	-	-	-	-
	SD	.	-	.	-	-	-	-	6.08	-
8	Mean	60.00	32.00	60.67	-	-	-	-	-	-
	SD	.	.	5.03	-	-	-	-	-	-
9	Mean	168.50	-	1215.00	-	-	-	67.00	-	-
	SD	176.07	-	.	-	-	-	-	-	-
10	Mean	59.00	-	204.00	-	-	-	-	-	-
	SD	21.21	-	8.49	-	-	-	-	-	-
11	Mean	44.00	60.00	178.00	50.00	32.00	-	55.00	-	-
	SD	62.23	39.60	67.43	39.60	.	-	14.14	-	-
12	Mean	1140.50	170.00	248.00	112.50	63.50	-	21.00	8.00	7.67
	SD	217.08	82.02	84.85	34.65	44.55	-	12.73	8.49	4.51
Total	Mean	227.36	77.07	289.61	108.50	53.00	4603.00	38.33	7.50	10.22
	SD	298.49	54.41	373.80	89.93	36.37	1749.38	24.85	5.54	5.93

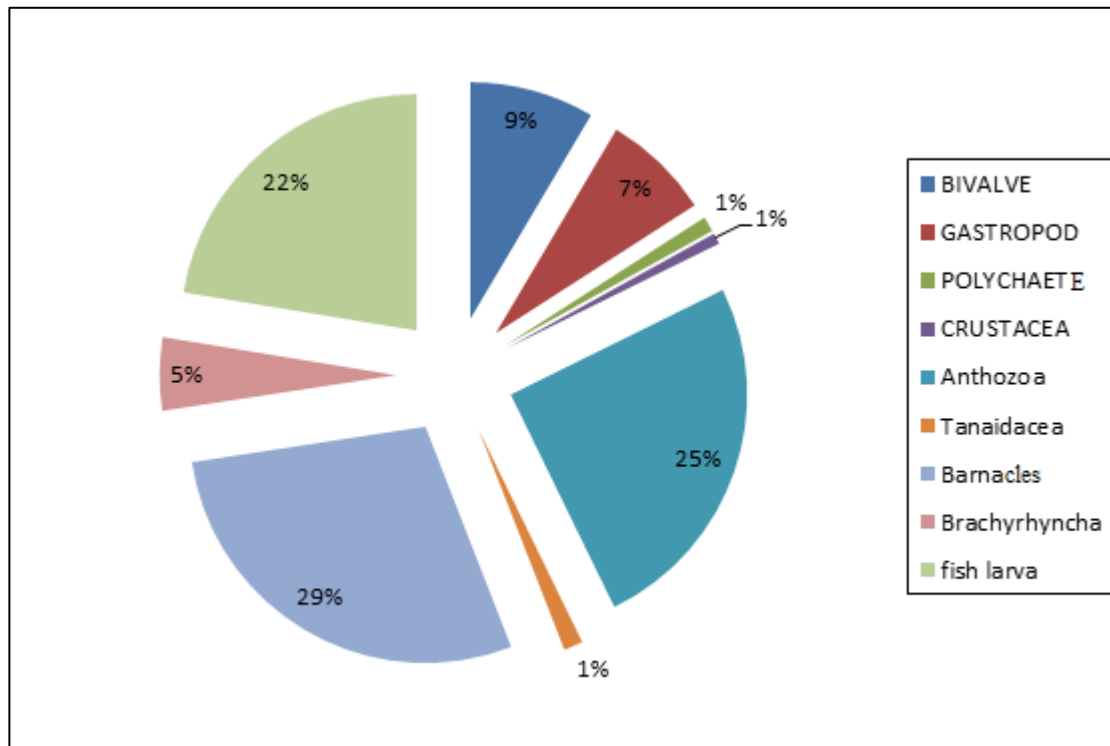
**Table 4.10.** Temporal distribution of macrofaunal taxa (individual/m<sup>2</sup>) over different time interval.

Time		Bivalve	Gastropod	Polychaet	Crustacea	Anthozoa	Tanaidacea	Barnacles	Brachyrrhyncha	Fishlarve
1	Mean	93.50	88.00	176.00	88.00	-	-	28.50	14.00	14.67
	SD	54.84	0.00	124.45	62.23	-	-	23.33	-	3.79
2	Mean	22.00	132.00	88.00	165.00	-	-	20.50	5.00	6.00
	SD	-	-	22.00	202.23	-	-	13.44	-	2.83
3	Mean	348.89	49.00	184.25	88.00	32.00	-	67.00	4.50	-
	SD	305.67	28.51	82.81	-	0.00	-	-	0.71	-
4	Mean	245.60	114.00	457.10	91.33	95.00	4603.00	65.00	8.50	9.00
	SD	382.28	83.15	526.24	40.67	-	1749.38	-	9.19	6.93
Total	Mean	227.36	77.07	289.61	108.50	53.00	4603.00	38.33	7.50	10.22
	SD	298.49	54.41	373.80	89.93	36.37	1749.38	24.85	5.54	5.93

In general, benthic organisms were identified according to O' dannel (1991) at the 12 sampling stations across 4 sampling periods (3 replicate). Individual species of Tanaeidae 36% of the total abundance followed by Polychaeta (23%) and Bivalve (18%), Crustacea constituted 8% and the rest of the macrobenthic spices (with low percentage) are shown in Fig.4.10. Moreover, Fig.4.11 is demonstrated the Box-Whisker plots of the spatial variation of benthic density (ind/m<sup>2</sup>) at different stations and during four times sampling.

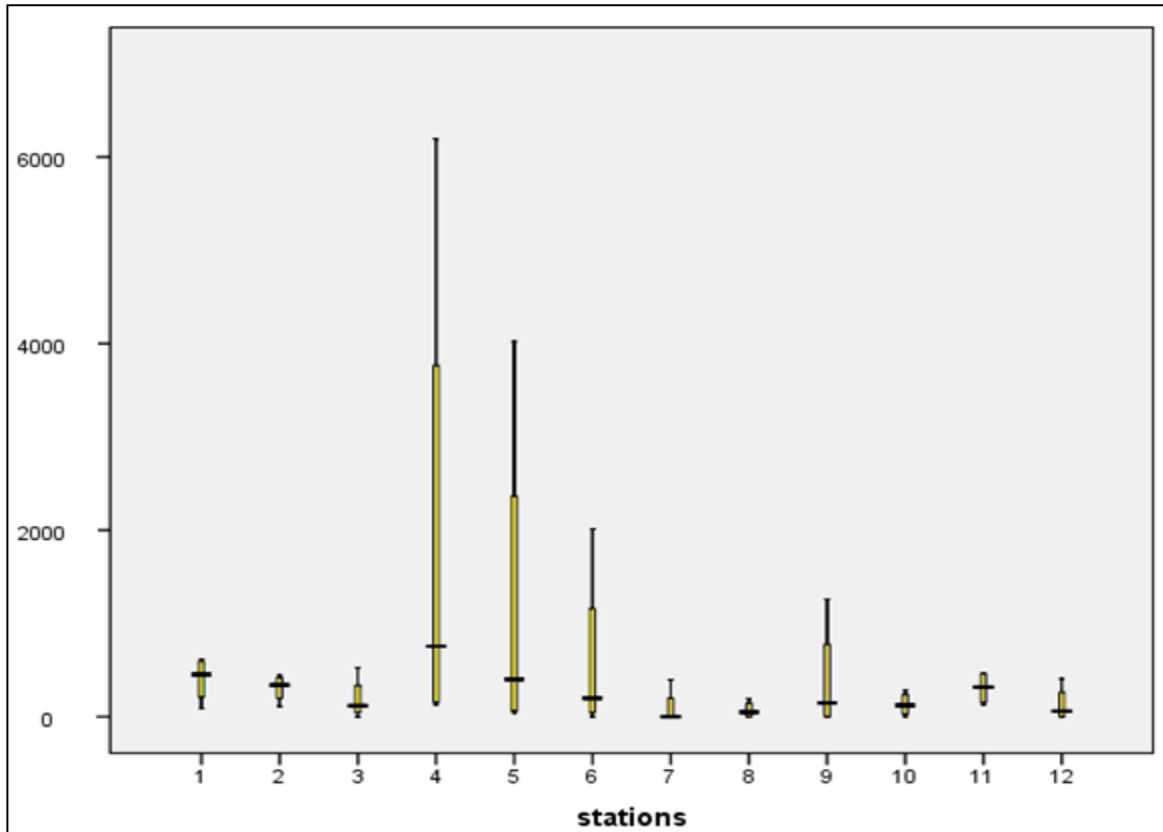


A.

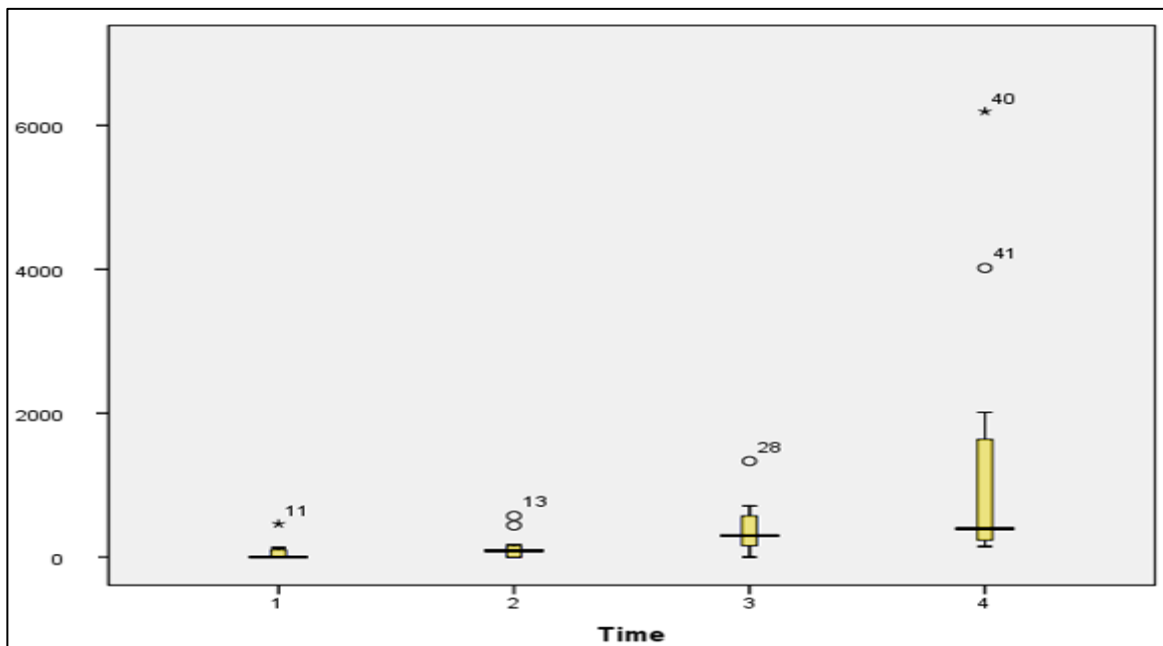


B.

**Fig.4.10. A.** Total density (ind/m<sup>2</sup>) of different macrobenthic during four sampling time  
**B.** Total biomass (g/m<sup>2</sup>) of different macro-benthic during four sampling times



A.



B

**Fig.4.11.** A. Box-Whisker plots of the spatial variation of benthic density (ind/m<sup>2</sup>) at different stations B. Box-Whisker plots of the spatial variation of benthic density (ind/m<sup>2</sup>) during four times sampling

In general, maximum abundance of Mollusca, Anthozoa and Gastropod (individual m<sup>2</sup>) was observed at station No.12 (7), Polychaeta (individual m<sup>2</sup>) at station No.6 (3-BI), Crustacea and Malacostraca at station No.4 (2-BI), Barnachel at station No.11 (6), Brachyryhyncha at station No.7 (4), Fishlarve at stations No.2 and No.3 (1-J and 2) and Tanaidacea at station No.2 and No.12 (1-J and 7).

**Table 4.11.** Results of Kruskal wallis analysis of differences in composition of macro-benthic community assemblages between stations and sampling time

	BIVALVE	GASTROPOD	POLYCHAET	CRUSTACEA	Anthozoa	Barnachel	Brachyryhyncha	Fishlarve
Chi-Square	8.09	4.44	5.51	0.14	2.00	3.86	0.99	1.88
df	3.00	3.00	3.00	3.00	1.00	3.00	3.00	2.00
Asymp. Sig.	0.04	0.22	0.14	0.99	0.16	0.28	0.80	0.39

a. Kruskal Wallis Test

b. Grouping Variable: sampling Time

	BIVALVE	GASTROPOD	POLYCHAET	CRUSTACEA	Anthozoa	Tanaidacea	Barnachel	Brachyryhyncha	Fishlarve
Chi-Square	13.055	11.545	16.593	5.167	.500	1.000	4.714	.245	5.542
df	11	8	11	4	1	1	3	2	3
Asymp. Sig.	.290	.173	.121	.271	.480	.317	.194	.885	.136

a. Kruskal Wallis Test

b. Grouping Variable: stations

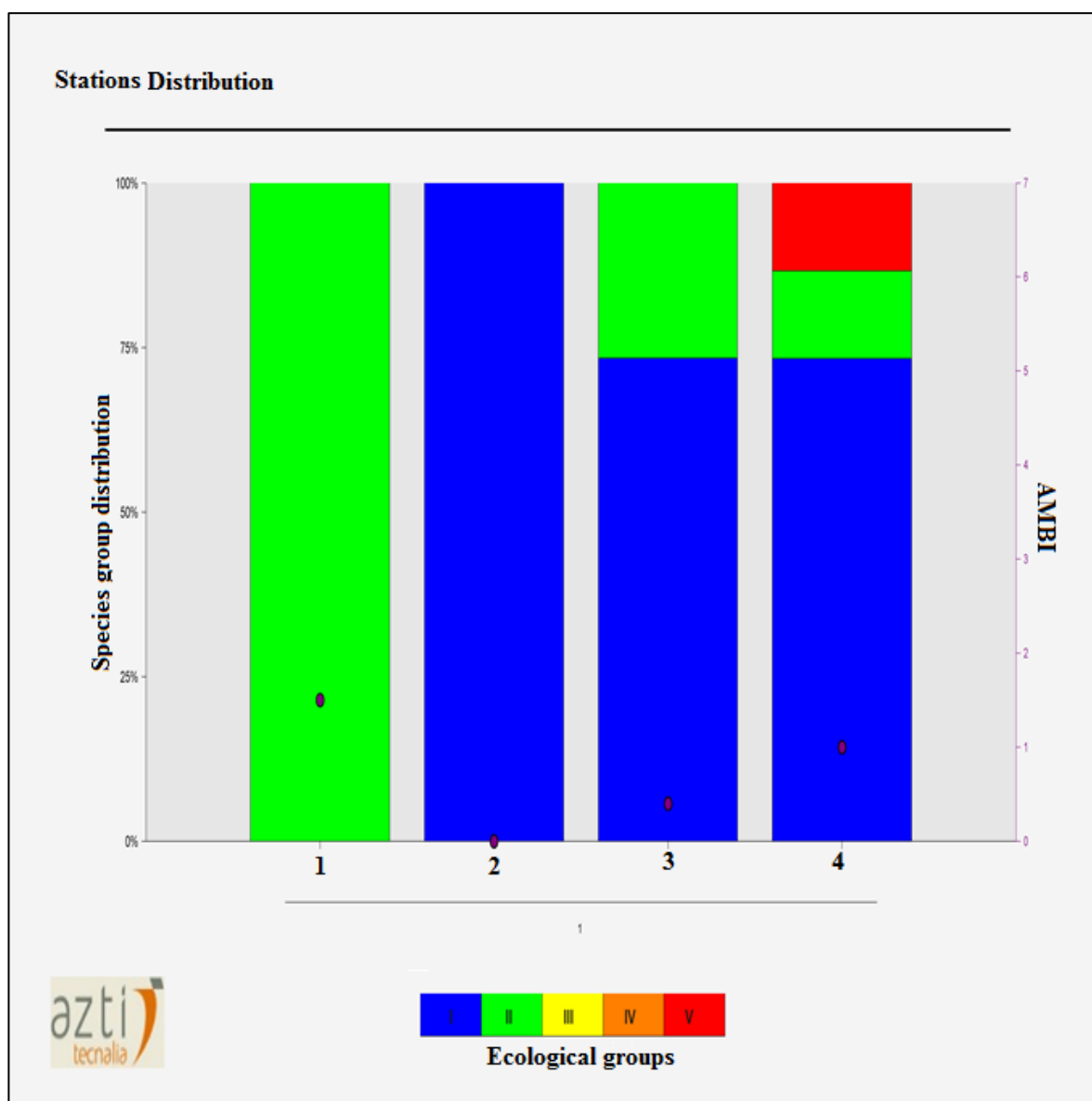
The results of Kruskal wallis analysis showed that , there was not any significant differences in composition of macro- benthic community assemblages and stations during the sampling times (Table 4.11).

Large standard deviations in the total number of individuals indicated that temporal changes or inter-replicate differences varied strongly. In temporal scale, Crustacea were dominant while Brachyryhyncha and fish larva showed the lowest concentration in all sampling periods. Moreover, Tanaidacea bears 36% of the macro-benthic community in this study. However, this ecological group (Tanaidacea) was not observed at more than half

of the stations. The largest macro-benthic group after Tanaidacea is Polychaeta which are bear 23% of this community.

Several ecological indices were applied to assess sediment quality based on the response of the soft-bottom macro benthic structure to changes in the environment. In this study, the AMBI was calculated (using the AMBI 4.0 program -[www.azti.es](http://www.azti.es)) based on the guidelines from the authors (using the July 2006 species list) (Borja and Muxika, 2005). Also the M-AMBI was calculated by factor analysis (FA) of AMBI, species richness (as number of taxa) and Shannon's diversity index values.

Benthic community was dominated by ecological group I and II (sensitive species) at stations No.1 and No.2 (1 and I-J); thus, they are classified as slightly polluted. While stations, such as No.6 and No.7 (3-BI and 4- in the vicinity of BI-PC effluent outlets) can be classified as heavily polluted and the benthic communities in these sites were dominated by ecological group V (opportunistic species). Also, ecological group III which are the tolerant species (to excess of organic matter enrichment) was observed at stations No.4 and No.5 (2-BI and 3); while ecological group IV (second order opportunist species) was not found in sampling stations (Fig.4.12 and Table 4.12).



**Fig.4.12.** Range of ecological group percentage for different sampling times

**Table 4.12.** Identified macrobenthic communities in Musa Bay sediment samples and their ecological groups according to Borja et al. (2000)

Biotic taxa			Groups
Polychaets	Syllidae	Syllis sp.	II
	Capittelidae	Capitella sp.	V
	Glyceridae	Glycera sp.	II
	Spoineidae		III
	Nereidae		III
	Orbinidae		III
Mollusk	Veneridae	Callista sp.	I
		Paphia sp.	I
		circenita callipyga	III
		Marcia hiantina	I
		Anachis misera	I
	Tellinidae		I
	Atyidae		II
	Naticidae		II
	Acmaeidae	Acmea sp.	*
	Phasciolaridae		*
	Collumbellidae	Coumbella sp.	I
Crustacean	Amphipoda	Caprella sp.	*
	Isopoda		I
	Tanaidae	Tanais sp.	*
	Brachiura		*
Turritellidae			*
Pennatulidae			*
Grapsidae			II
Antozoa			I
Atyidae			I
Fish Larva			*

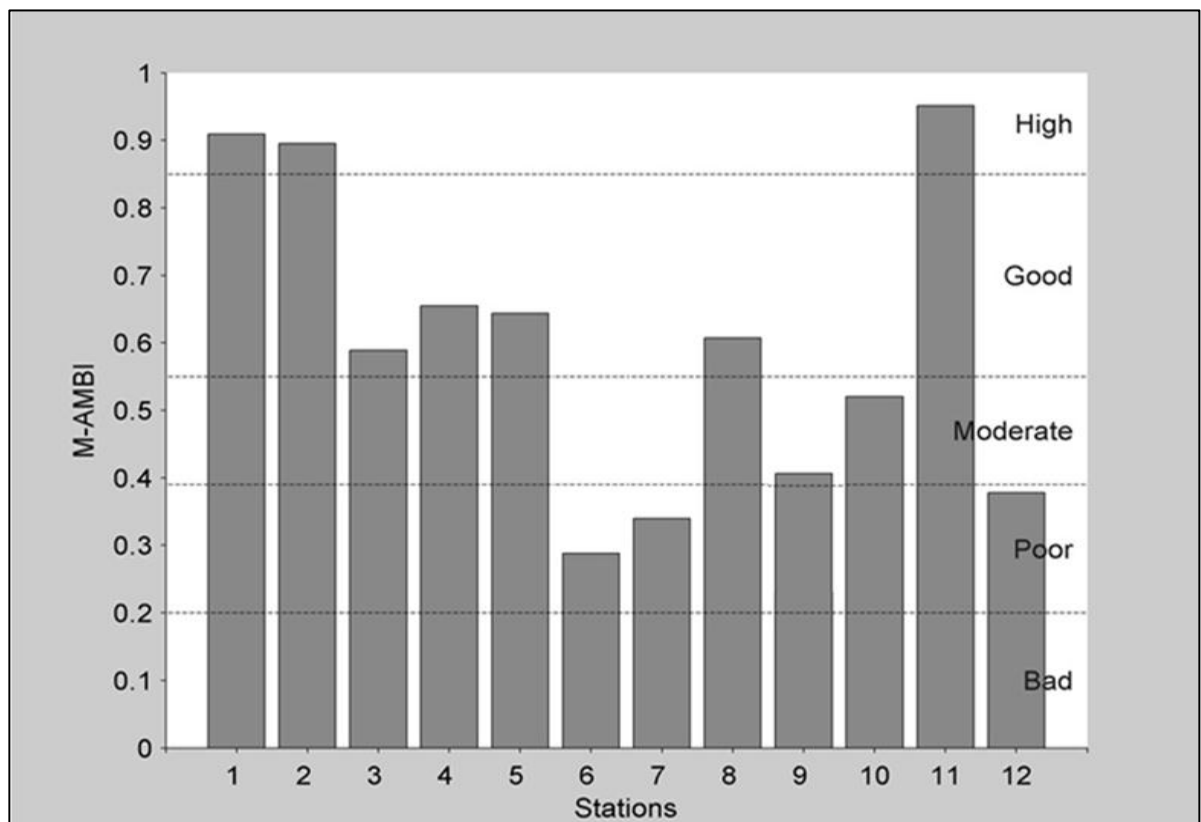
\* Not assigned

In total, the average value of AMBI was 2.66, so it can be categorized as slightly polluted. The pollution level of most of the stations varied between undisturbed and moderately polluted (except stations No.6 and No.7 which are heavily polluted- in the vicinity of BI-PC effluent outlets). According to AMBI, High condition belonged to station No.2 (1-J) and the bad condition was observed at station No.7 (4: in the vicinity of BI-PC Aromatic effluent outlet) (AMBI: 6, diversity and richness: 0) (Table4.13).



**Table4.13.** Results of the AMBI, diversity and richness values, by sampling station, together with the selection of ‘High’ and ‘Bad’ reference conditions, for the M-AMBI (Borja et al., 2000; Borja and Muxika, 2005)

Stations No.	1	2	3	4	5	6	7	8	9	10	11	12
Station name	1	1-J	2	2-BI	3	3-BI	4	4-BI	5	5-R	6	7
I(%)	77	90.7	51.2	88.1	83.3	20.8	34.3	33.6	21.7	22	40.7	24.3
II(%)	19.9	9.3	0	8.9	9.6	8.4	8.6	55.5	4.6	49	51.3	27.5
III(%)	0	0	0	0.4	0.9	0	0	0	0	0	4.9	0
IV(%)	0	0	0	0	0	0	0	0	0	0	0	0
V(%)	3	0	48.8	2.6	6.1	70.7	57.1	10.9	73.7	29	3	48.2
Mean AMBI	0.725	0.107	4.439	2.135	3.066	5.146	6.139	4.191	4.884	4.836	1.167	4.976
BI from Mean AMBI	1	0	4	2	2	5	6	3	4	4	1	4
Disturbance Classification	Undisturbed	Undisturbed	Moderately disturbed	Slightly disturbed	Slightly disturbed	Heavily disturbed	Heavily disturbed	Moderately disturbed	Moderately disturbed	Moderately disturbed	Undisturbed	Moderately disturbed
Richness	13	12	10	13	13	5	4	9	4	8	15	5
Diversity	3.42	3.24	2.68	1.79	1.9	1.51	1.37	2.98	1.13	2.66	3.56	2.05
M-AMBI	0.90	0.89	0.58	0.65	0.64	0.27	0.33	0.60	0.41	0.52	0.95	0.37
status	High	High	Good	Good	Good	Poor	Poor	Good	Poor	Moderate	High	Poor



**Fig.4.13.** M-AMBI plots of sampling station

The results of M-AMBI are shown in Figure 4.13. Owing to this figure and Table 4.12, most of the stations were above the moderate status except stations No.6, 7 and 12 (3-BI, 4 and 7, respectively).

According to the Bray-Curtis index for similarities based on macrobenthic abundance, all of the stations showed less than 50% similarity for abundance except stations 3-BI and 4. The range of Shannon diversity index was 1.13 (at station 5) to 3.56 (at station 6) and Richness indices values were 4 to 15. The Shannon index value was above 3 at stations 1, 1-J and 6.

Other analysis that can help to assess benthic respond to contaminant is correlation analysis. In this research there was a significant negative correlation between Polychaeta, Tanaidacea, Brachyrehincha and Fish larva ( $r = -1$ ,  $r = -1$  and  $r = -0.999$  respectively). Also there was a negative correlation between the distributions of Crustacea, Tanaidacea and TPH ( $r = -0.845$ ,  $r = -1$  and  $r = -1$  respectively). Moreover, there was a significant negative correlation between Tanaidacea and PAHs ( $r = -1$ ) (Table 4.14).

**Table 4.14.** Correlation coefficient between benthic communities, TPH and PAHs in the sediment samples of the Bay

		Bivalve	Gastropod	Polychaet	Crustacea	Anthozoa	Tanaidacea	Barnachel	Brachyrrhyncha	Fishlarve	TPH	PAH
Bivalve	Pearson Correlation	1.00										
	Sig. (2-tailed)											
Gastropod	Pearson Correlation	0.541*	1.00									
	Sig. (2-tailed)	0.05										
Polychaet	Pearson Correlation	-0.03	0.07	1.00								
	Sig. (2-tailed)	0.91	0.83									
Crustacea	Pearson Correlation	0.46	1.000**	0.69	1.00							
	Sig. (2-tailed)	0.54	.	0.20								
Anthozoa	Pearson Correlation	0.70	0.91	0.96	1.000**	1.00						
	Sig. (2-tailed)	0.51	0.27	0.17	.							
Tanaidacea	Pearson Correlation	0.91	0.01	-1.000**	0.46	-0.30	1.00					
	Sig. (2-tailed)	0.27	-0.36	.	0.54	0.44						
Barnachel	Pearson Correlation	0.76	-1.000**	0.72	-0.46	0.46	-0.25	1.00				
	Sig. (2-tailed)	0.46	.	0.49	0.06	0.64	0.28					
Brachyrrhyncha	Pearson Correlation	-0.74	-0.90	-1.000**	-0.15	0.56	0.79	0.70	1.00			
	Sig. (2-tailed)	0.47	0.10	.	0.44	0.74	0.46	0.51				
Fishlarve	Pearson Correlation	-0.58	-0.90	-.999*	-0.26	0.36	-0.25	0.05	1.000**	1.00		
	Sig. (2-tailed)	0.23	0.10	0.03	0.53	0.64	0.24	0.97	.			
TPH	Pearson Correlation	-0.20	0.08	-0.25	-.845**	0.96	-1.000**	-0.50	0.41	0.55	1.00	
	Sig. (2-tailed)	0.30	0.79	0.24	0.01	0.19	.	0.31	0.42	0.13		
PAH	Pearson Correlation	-0.15	-0.46	-0.03	-0.26	-0.34	-1.000**	0.74	0.06	0.64	-0.03	1.00
	Sig. (2-tailed)	0.44	0.09	0.91	0.53	0.78	.	0.09	0.92	0.06	0.85	

\*, Correlation is significant at the 0.05 level (2-tailed).

\*\*, Correlation is significant at the 0.01 level (2-tailed).

Moreover, the two way ANOVA analysis based on macro-benthic abundance in sampling stations showed that, there is not any significant difference between them ( $p > 0.05$ ), except Mollusca ( $p = 0.00 < 0.05$ ).

#### 4.1.7. Physical Parameters of Musa Bay Water

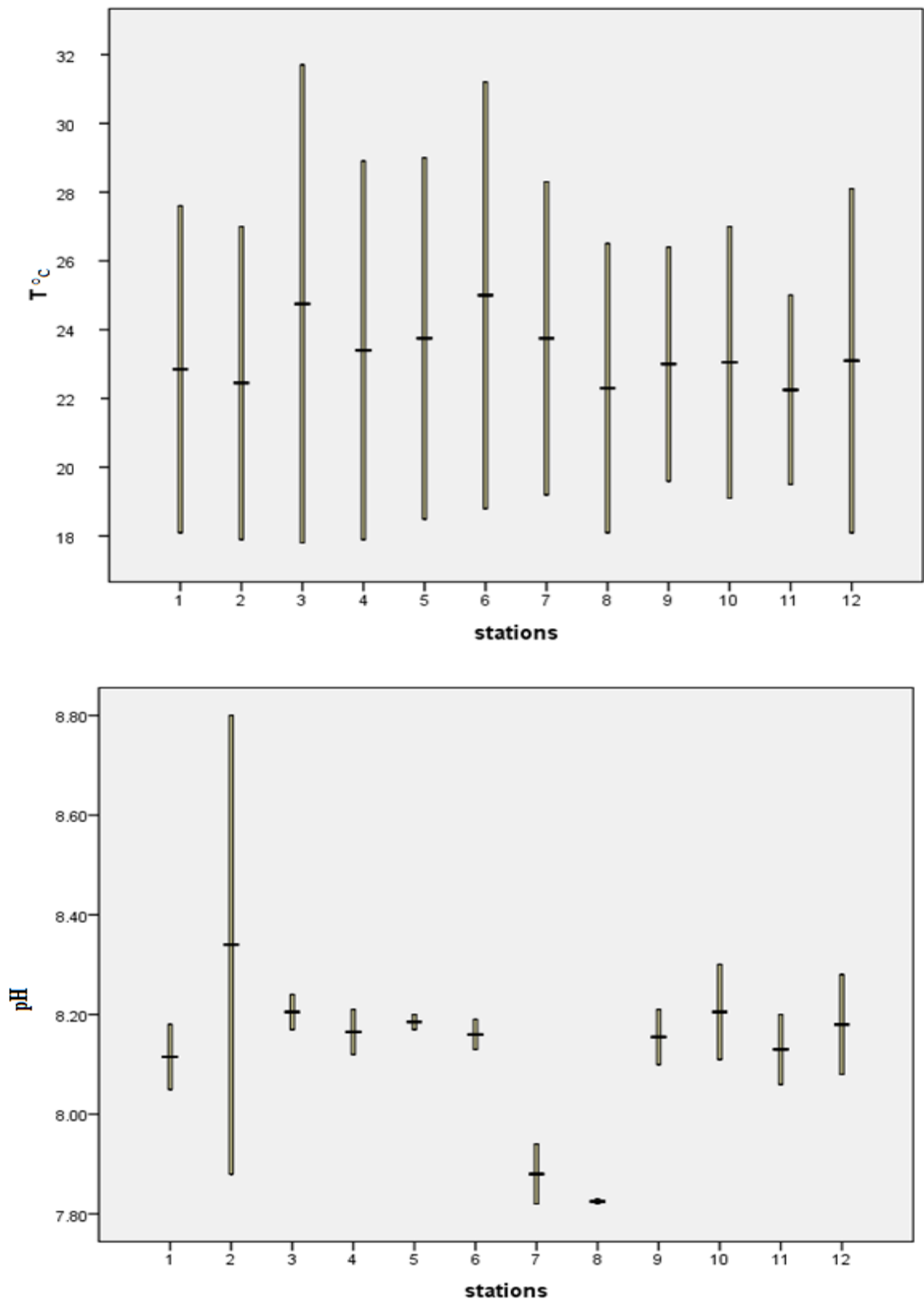
During four season sampling , the water temperature of the Bay was fluctuate between 15.80 °C to 35.60°C and pH during 4 times sampling was between 7.82 to 8.80. dissolved oxygen which is the most important factor in aquatic ecosystems, fluctuated in the water of the Bay between 4 mg/l and 6.80 mg/l (Max: at station No.12). The average

concentration of aforementioned factors and other related parameters in the study area, are shown in Table 4.15. Moreover, statistical description of physical parameters is shown in AppendixI.

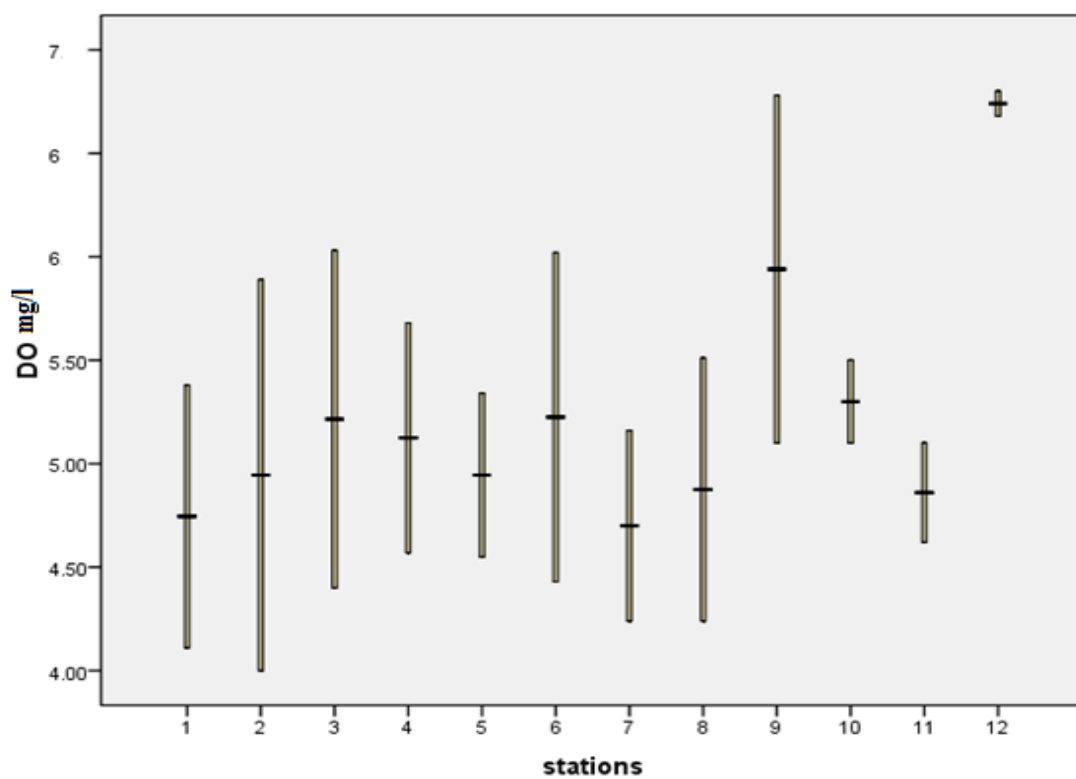
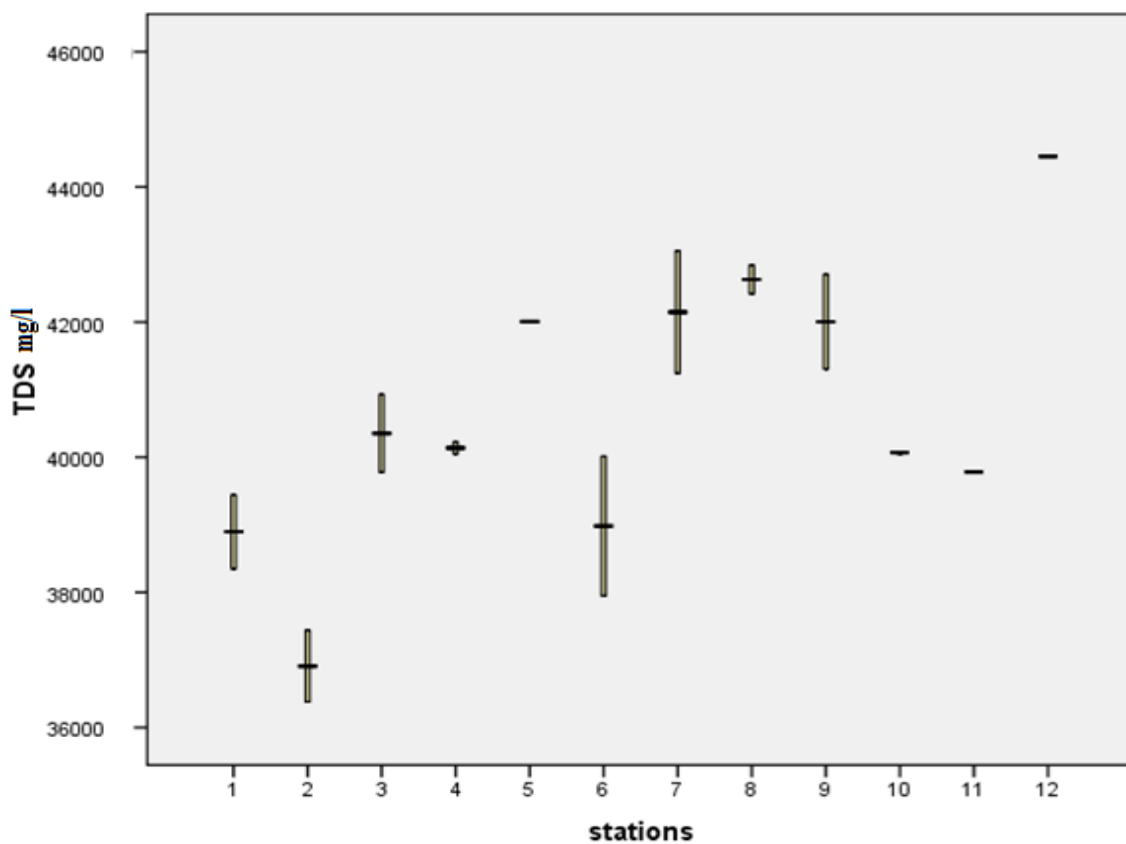
**Table 4.15.** Values of mean, minimum and maximum of physical parameters of surface water in Musa Bay sampling stations

parameter	Mean	Std. Deviation	Minimum	Maximum	Percentiles		
					25th	50th (Median)	75th
<b>T</b>	23.30	5.06	15.80	31.70	16.20	22.30	27.97
<b>pH</b>	8.12	0.20	7.82	8.80	8.05	8.15	8.20
<b>TDS</b>	4.06	2061.63	36380.00	44450.00	3.97	40154.00	4.23
<b>EC</b>	5.90	2349.88	53500.00	63500.00	5.81	59050.00	6.04
<b>DO</b>	5.21	0.84	4.00	6.80	4.46	5.13	5.83
<b>Salinity</b>	55.58	77.92	36.50	421.30	38.80	39.15	41.27

The Two-Way ANOVA analysis showed significant difference ( $P < 0.05$ ) only in concentration of TDS (mg/l) in different stations and also during the sampling period. Figure 4.14 shows the Box-Whisker plots of the spatial variation of some physical water parameters in sampling stations with the minimum and maximum concentration; the line of each plot is the mean value.

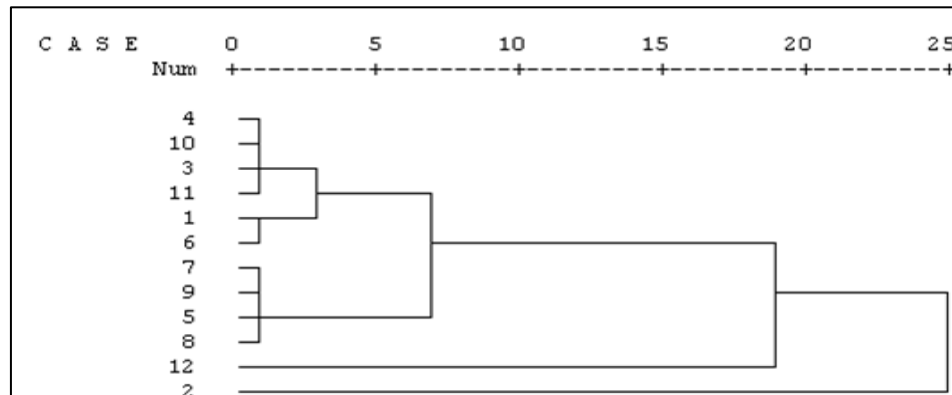


**Figure 4.14.** Box-Whisker plots of the spatial variation of  $T^{\circ}\text{C}$ , pH, TDS mg/l, and DO mg/l in 12 sampling stations of Musa Bay



**Figure 4.14.** (Continued) Box-Whisker plots of the spatial variation of T °c, pH, TDS mg/l, and DO mg/l in 12 sampling stations of Musa Bay

There was a significant negative correlation between temperature and dissolved oxygen ( $r=-0.065$ ,  $p<0.001$ ); But in general, all of the stations were over saturated with oxygen during this period.



**Fig.4.15.** Cluster analyses to classify of different stations based on physical parameters

The cluster shows three significant groups and indicated that station 2 and 12 are completely separated from other stations (Fig.4.15).

According to water quality score (WQS) for coastal waters based on (SCECAP, 2001) scores (Van Dolah et al., 2004), the average concentration of dissolved oxygen in the study area was more than 4 (mg/l); and other parameter is pH which was greater than 7.4. Thus, these parameters are meat the scores of WQS.

## 4.2. Wastewater Analysis

### 4.2.1. Total Petroleum Hydrocarbon

The concentrations of TPH obtained in the present investigation are shown in Table 4.15.

**Table 4.16.** TPH concentration (mg/l) in the wastewater discharges of PETZONE petrochemical companies

No.	Station	Mean	Minimum	Maximum	Effluent Limit based on Daily maximum <sup>1,2</sup>	Effluent Limit based on Daily maximum <sup>3,4</sup>
1	AK-PC	2.19	0.10	5.26	10	5
2	BI-PC 2	20.13	17.60	22.66	10	5
3	BI-PC 1	13.10	10.19	20.00	10	5
4	ETP1	1.70	0.10	4.00	10	5
5	ETP2	2.13	0.10	7.83	10	5
6	EX-TANK	2.13	0.06	6.40	10	5
7	F-PC	2.21	0.10	8.10	10	5
8	FA-PC	4.36	0.10	17.00	10	5
9	FR-PC	2.35	0.12	4.20	10	5
10	GH-PC	3.27	0.10	10.15	10	5
11	K-PC	1.05	0.07	4.40	10	5
12	Kz-PC	2.52	0.97	4.07	10	5
13	M-PC	3.14	0.91	5.33	10	5
14	R-PC	17.64	10.56	35.33	10	5
15	SB-PC	2.95	0.10	6.83	10	5
16	Treatment Plant (site 1)	1.98	0.10	5.85	10	5
17	ST-PC	7.57	2.00	10.93	10	5
18	STET	0.64	0.10	1.76	10	5
-	Total	4.61	0.06	35.33	-	-

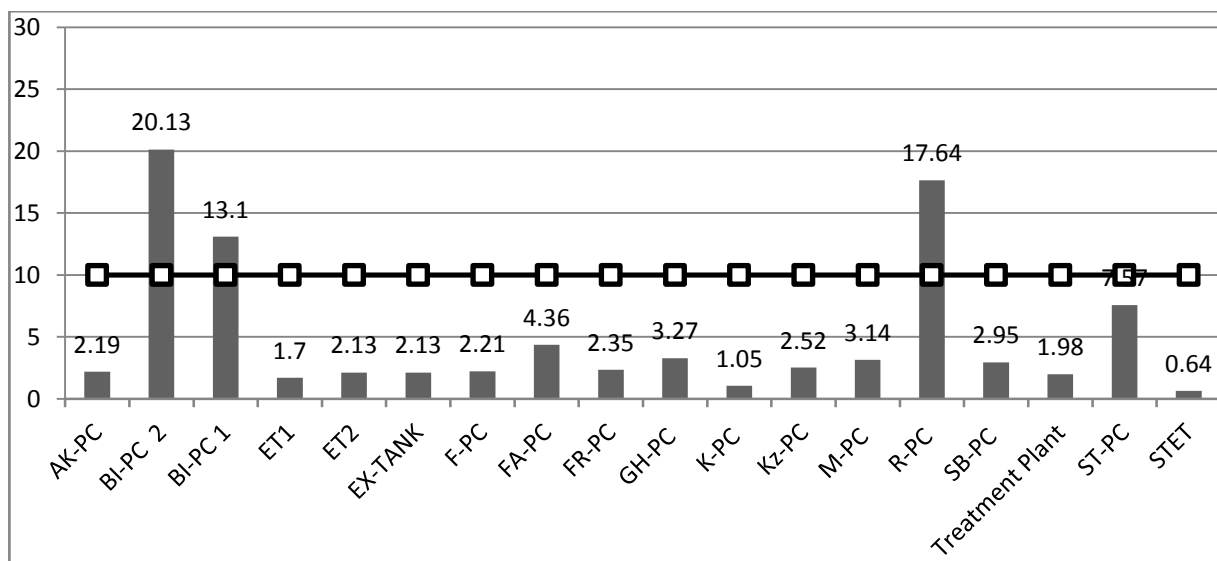
More than 10 mg/l or 5 mg/l



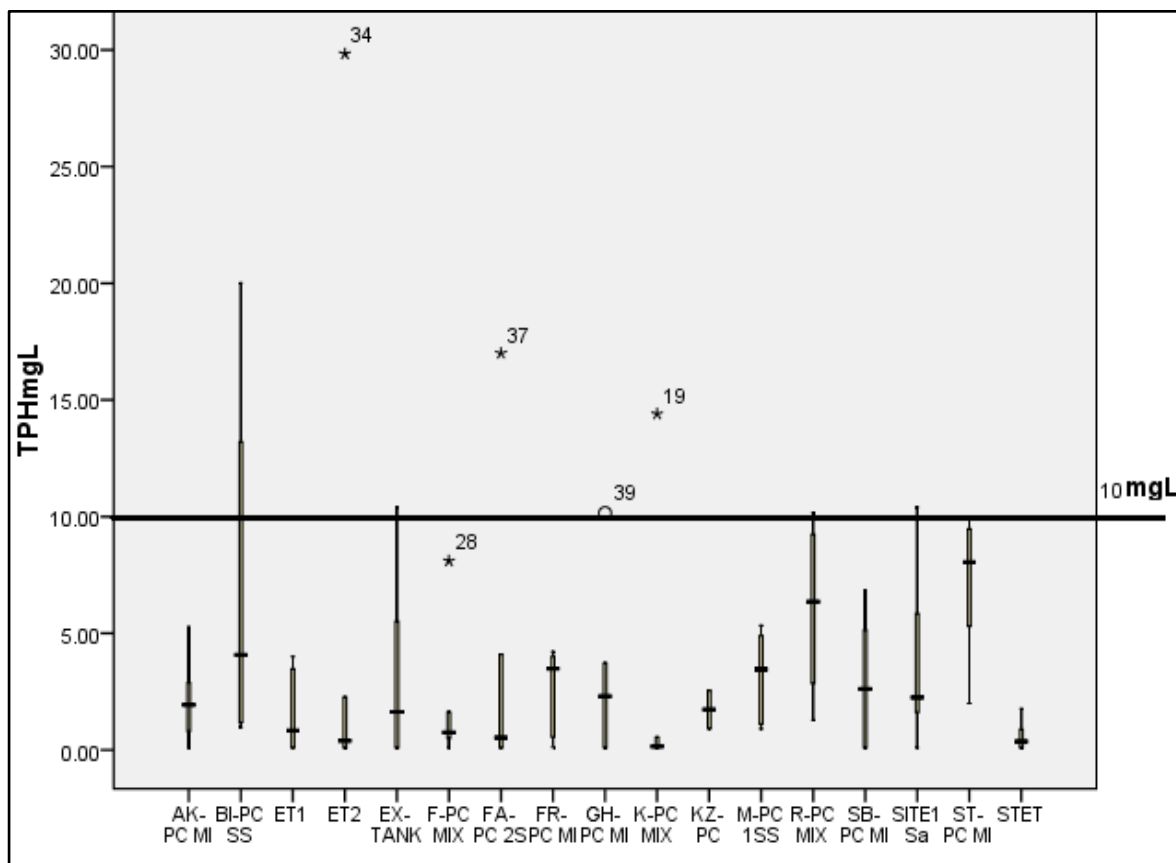
<sup>1</sup> (UWI, 2004) ; <sup>2</sup>(EHS, 2010) ; <sup>3</sup> (US.EPA, 1995); <sup>4</sup>(US.EPA New England, 2010)

The average TPH concentration in wastewater samples was 4.61 (mg /l), with a range of 0.06 to 35.33 (mg/l), as shown in above mentioned table.





A.

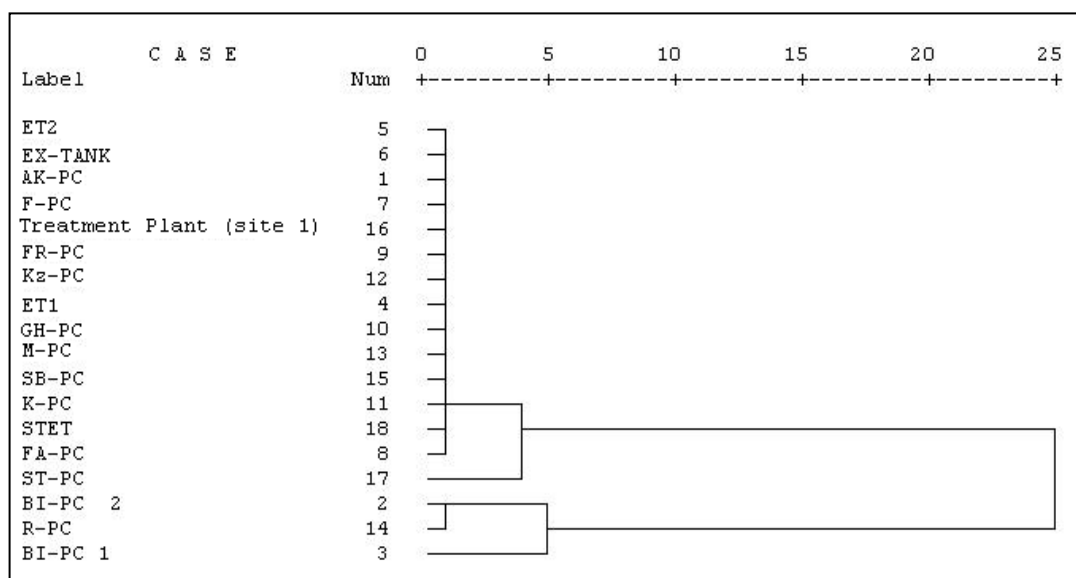


B.

**Fig.4.16. A.** The average Concentration of TPH (mg/l) at sampling stations  
**B.** Box-Whisker plots of the spatial variation of TPH at sampling stations (the guideline is 10 mg/l)

Based on Figure 4.16, all of the stations, the average concentration of TPH was lower than the guideline value (10 mg/l), with the exception of three sampling stations labeled as follows: BI-PC1, BI-PC2 and R-PC. These stations are related to Bandar-e-Imam Khomeini petrochemical company and Razi petrochemical company, respectively. The products Razi Petrochemical Company produces are: natural condensate, sulphuric acid, Di ammonium phosphate, granulated sulphur, Ammonia, urea and phosphoric acid<sup>1</sup> and the Imam Khomeini petrochemical company produces are : aromatics, polymers, chemicals, and fuel<sup>2</sup>.

The average cluster analysis results for TPH demonstrated two significant groups which are station 3, 14 and 2 (BI-PC 1, R-PC and BI-PC 2 respectively) as group 1 and ST-PC (station No.17) as group 2 (Fig.4.17).



**Fig.4.17.**A dendrogram representation of a hierarchical cluster analysis of the TPH

<sup>1</sup> <http://www.razip.com>

<sup>2</sup> <http://www.bipc.org/>

Thus, the cluster analysis indicated that ST-PC which is related to the Shahid Tondgoyan petrochemical company cannot be categorized in the group of other stations. The products of this company are: Shahid Tondgoyan petrochemical company produces PET (bottle grade, textile grade and film grade), amorphous-grade polyethylene terephthalate (amorphous chips) and purified terephthalic acid (PTA)<sup>1</sup>.

Due to the closeness of Bandar-e-Imam Khomeini and Razi petrochemical companies and their direct discharge to Musa Bay; the high concentrations of TPH in their effluent outlets may have adverse impacts on the aquatic ecosystem of the bay. Thus, the concentration of polycyclic aromatic hydrocarbons was monitored in the sampling wastewaters too.

#### **4.2.2. Polycyclic Aromatic Hydrocarbon**

The concentrations of PAHs obtained in this study and related effluent limit guidelines are shown in Table 4.16.

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<sup>1</sup> <http://www.stpc.ir/fa/main/default.aspx>

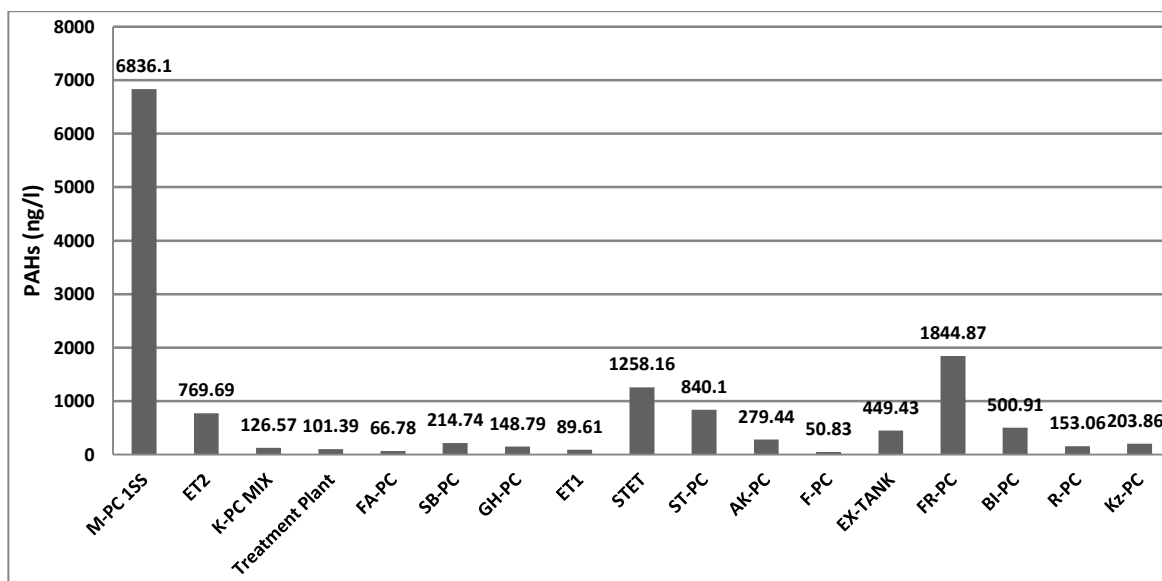
**Table4.17.**Concentrations of PAHs (ng/l) in the effluents of selected petrochemical companies

No.	Station	$\Sigma$ PAH mean (ng/l)	$\Sigma$ PAH(ngL) mean ( $\Sigma$ Group I ng/l)	Effluent Limit ( $\Sigma$ Group I ng/l) <sup>1</sup>	$\Sigma$ PAH(ngL) mean ( $\Sigma$ Group II ng/l)	Effluent Limit ( $\Sigma$ Group I ng/l) <sup>1</sup>
1	M-PC	6836.10	355.01	10000	6481.09	100000
2	ET2	769.69	100.22	10000	669.47	100000
3	K-PC	126.57	9.44	10000	117.13	100000
4	Treatment Plant (site 1)	101.39	36.66	10000	64.72	100000
5	FA-PC	66.78	6.40	10000	60.37	100000
6	SB-PC	214.74	24.98	10000	189.75	100000
7	GH-PC	148.79	32.14	10000	116.64	100000
8	ET1	89.61	10.13	10000	79.48	100000
9	STET	1258.16	3.57	10000	1254.58	100000
10	ST-PC	840.10	229.76	10000	610.32	100000
11	AK-PC	279.44	39.62	10000	239.81	100000
12	F-PC	50.83	3.311	10000	47.51	100000
13	EX-TANK	449.43	20.82	10000	428.61	100000
14	FR-PC	1844.87	76.716	10000	1768.15	100000
15	BI-PC	500.91	14.9	10000	486.00	100000
16	R-PC	153.06	219.95	10000	149.44	100000
17	Kz-PC	203.86	2.23	10000	201.62	100000
Total	-	13934.32	1185.88	10000	12964.78	100000

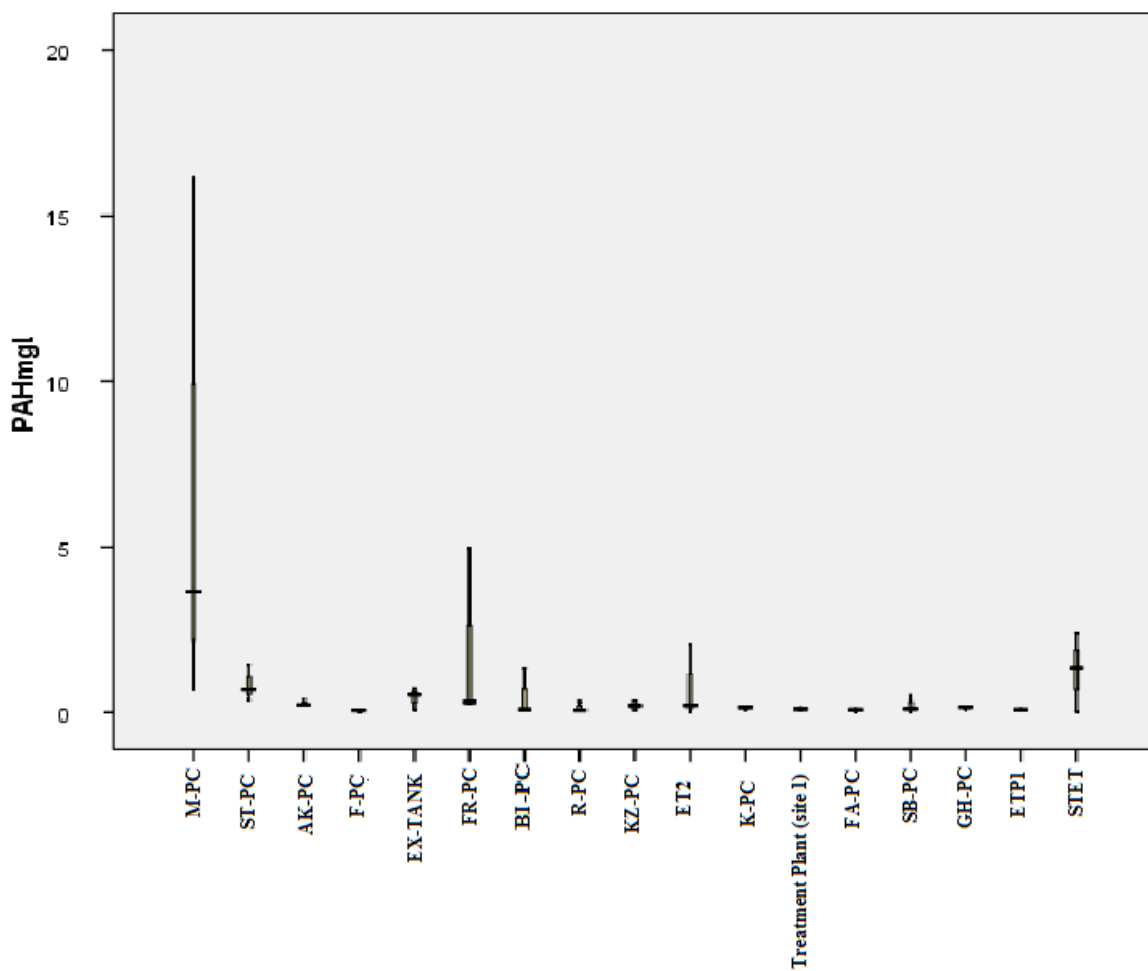
- Group I PAHs: a. Benzo(a) Anthracene, b. Benzo(a) Pyrene, c. Benzo(b)-Fluoranthene, d. Benzo(k)Fluoranthene, e. Chrysene, f. Dibenzo(a,h) Anthracene, g. Indeno(1,2,3-cd) Pyrene
- Group II PAHs: a. Acenaphthene, b. Acenaphthylene, c. Anthracene, d. Benzo(ghi)-Perylene, e. Fluoranthene, f. Fluorene, g. Naphthalene, h. Phenanthrene, i. Pyrene (US EPA New England, 2010)

The average concentrations of  $\Sigma$ PAHs group I and group II (based on the guidelines) were 1.185 and 12.965 ( $\mu\text{g/l}$ ) which means it still meets the guideline. Also the average concentration of  $\Sigma$ PAHs was 819.66 (ng/l) and ranged from 50.83 to 6836.10 (ng/l), as shown in Table 4.17.

Moreover, according to the guideline, concentration of Acenaphthene more than 0.02  $\mu\text{g/g}$  in marine water column, can cause a stress in marine aquatic ecosystems. Thus, the concentrations of Acenaphthene in sampling stations are shown in Table4.10 (Table4.12) (ANZECC, 1992).



A.



B.

**Fig.4.18. A.** Average concentration of PAHs (ng/l) in the selected sampling stations  
**B.** Box-Whisker plots of the spatial variation of PAHs at sampling stations

**Table 4.18.** Average concentrations of Acenaphthene in sampling stations

NO.	Station	Acenaphthene $\mu\text{g/g}$
1	M-PC	0.42
2	ET2	0.01
3	K-PC	0.00
4	Treatment Plant (site 1)	0.00
5	FA-PC	0.01
6	SB-PC	0.00
7	GH-PC	0.00
8	ETP1	0.00
9	STET	0.00
10	ST-PC	0.02
11	AK-PC	0.04
12	F-PC	0.00
13	EX-TANK	0.01
14	FR-PC	0.05
15	BI-PC	0.01
16	R-PC	0.00
17	KZ-PC	0.01

As it shown in Table 4.18, the concentration of Acenaphthene was lower than the guideline value at all the sampling stations (guideline value: 100000  $\mu\text{g/g}$  – daily discharge value) (U.S.EPA, 1995; US EPA New England, 2010).

However, when effluents measured at the "end of pipe", it means that they were measured before releasing into the Bay, thus they are subsequently diluted in the Bay. Therefore, if the discharge concentration of PAHs is more than the guideline, it does not necessarily have a significant risk or it does not indicate that it may be contributing to a water quality standard exceedance in Musa Bay.

#### **4.2.3. Other Physicochemical Parameter of Wastewater**

The other parameters that were monitored in the wastewater of sampling stations were T ( $^{\circ}\text{C}$ ) , pH , EC ( $\mu\text{S}/\text{cm}$ ), TDS (mg/l) and COD (mg/l). in addition to TPH and PAHs , the concentration of COD was monitored in the sampling wastewaters; because, wastewater is typically distinguished by high levels of COD (Xiong, Strunk, Xia, Zhu, & Karlsson, 2001).

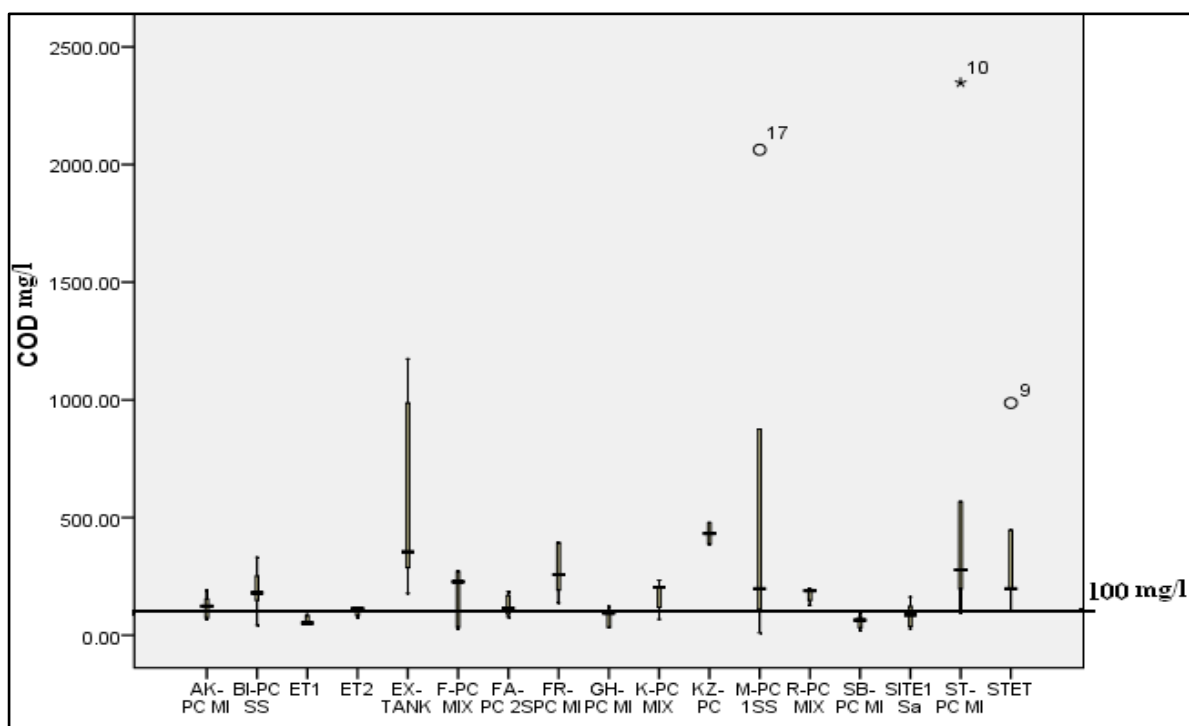
The average concentration of aforementioned parameters is shown in Table 4.19. The concentrations of COD (mg/l) in wastewater samples, which is an appropriate index that can represent the strength of a pollutant in samples, were greater than the guideline value at most of the stations (except stations, ET1, GH-PC, SB-PC and SITE : <100 mg/l) , also concentration of DO and TDS was lower than 3 (mg/l) and more than 1500 (mg/l) at most of the stations, respectively. But the effluents temperature at all of the stations meet the guideline value except at station AK-PC ( $T^{\circ}\text{C} < 35$ ). The maximum pH was observed at station K-PC, also the pH value was more than the guideline value at stations GH-PC and BI-PC, and other stations meet the guideline value. TDS values ranged from 792.1 to 23645.9 (mg/l), and the highest concentration of TDS was observed at BI-PC station which was much greater than the end of pipe guideline value (pH: 6-9).

**Table4.19.** Average concentration of T (°c) ,pH, EC (µs /cm), TDS (mg/l), COD (mg/l) and DO (mg/l) in selected samples

Parameter		COD	DO	EC	TDS	T	pH
Guideline	Stations	100 <sup>1</sup>	>3 <sup>1</sup>	-	1500 <sup>1</sup>	35 <sup>1</sup>	6-9 <sup>1</sup>
M-PC	Mean	651.40	2.88	3184.40	1789.56	32.08	7.74
	SD	859.24	1.17	2679.49	1673.55	4.00	1.20
ET2	Mean	100.40	3.27	2345.20	1253.26	28.27	7.84
	SD	20.42	1.82	940.47	537.65	3.23	0.61
K-PC	Mean	166.00	3.26	8721.00	5368.24	27.94	10.53
	SD	69.65	1.38	10302.52	6699.67	4.60	1.66
Treatment Plant (site 1)	Mean	87.40	4.28	8280.00	5070.56	28.72	7.09
	SD	56.58	1.49	12037.38	7831.22	4.81	0.40
FA-PC	Mean	127.40	1.98	2533.60	1442.10	33.57	8.03
	SD	48.24	1.38	2359.04	1481.98	5.20	0.48
SB-PC	Mean	57.00	4.13	2814.00	1575.11	28.50	8.13
	SD	31.62	2.18	1915.16	1210.44	6.58	0.39
GH-PC	Mean	75.80	2.91	1777.80	961.39	29.53	10.00
	SD	40.95	0.84	1692.03	965.32	3.95	1.25
ET1	Mean	66.75	2.21	3455.00	1921.04	28.45	7.64
	SD	21.33	1.21	1084.16	669.19	3.19	0.58
STET	Mean	385.40	2.92	4868.00	2815.64	29.80	8.80
	SD	359.81	2.10	2088.75	1292.83	4.60	0.28
ST-PC	Mean	697.10	3.34	1507.50	792.19	30.46	7.23
	SD	939.36	2.16	575.35	320.24	3.80	2.04
AK-PC	Mean	121.60	3.41	3600.60	2061.16	33.53	8.28
	SD	52.39	1.87	2704.06	1668.01	4.02	1.00
F-PC	Mean	166.30	3.67	2799.00	1534.14	26.68	8.10
	SD	125.82	2.30	1361.71	761.34	3.32	0.77
EX-TANK	Mean	190.60	2.58	36971.00	23645.92	29.12	9.10
	SD	108.30	0.36	30000.80	19583.32	6.43	2.60
FR-PC	Mean	596.00	2.71	20244.00	13115.10	30.04	7.54
	SD	451.59	1.53	20955.04	14469.88	6.46	1.75
BI-PC	Mean	171.00	1.43	6964.05	4143.81	28.80	8.31
	SD	31.75	1.39	3239.75	2051.55	2.62	1.50
R-PC	Mean	275.00	2.47	10514.60	6375.08	27.99	8.17
	SD	116.23	0.97	8789.09	5576.98	0.92	1.40
Kz-PC	Mean	432.50	2.82	6280.00	3684.00	28.45	8.08
	SD	64.35	0.74	5487.15	3411.08	1.63	0.33
Total	Mean	252.77	2.96	7505.59	4593.77	29.56	8.28
	SD	381.00	1.60	12767.20	8360.67	4.41	1.46

Did not meet the guideline value  (EHS, 2010; UWI, 2004)<sup>1</sup>





**Fig.4.19.** Box-Whisker plots of the spatial variation of COD (mg/l) at sampling stations

**Table 4.20.** Correlation coefficient between physicochemical parameters of wastewater

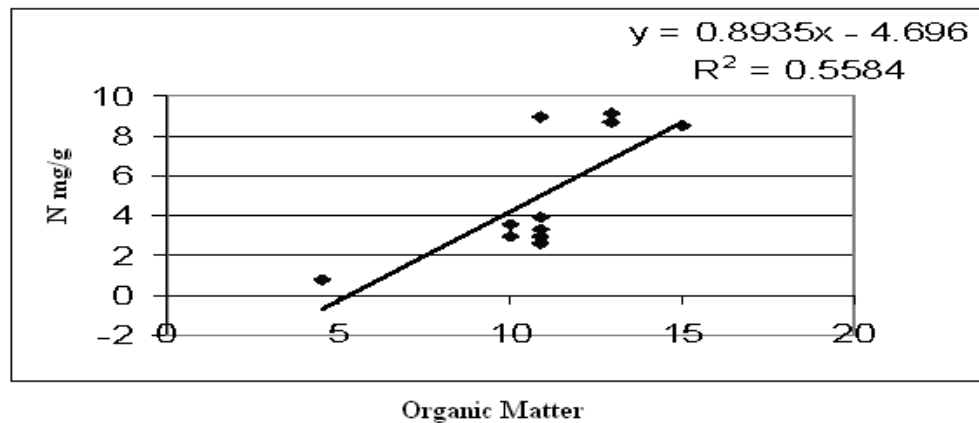
		COD	DO	TDS	pH	T
<b>COD</b>	Pearson Correlation	1				
	Sig. (2-tailed)					
<b>DO</b>	Pearson Correlation	-0.21	1			
	Sig. (2-tailed)	0.05				
<b>TDS</b>	Pearson Correlation	-0.02	0.01	1		
	Sig. (2-tailed)	0.84	0.96			
<b>pH</b>	Pearson Correlation	-0.18	0.19	0.31	1	
	Sig. (2-tailed)	0.10	0.07	0.01		
<b>T</b>	Pearson Correlation	0.15	-0.27	0.09	0.04	1
	Sig. (2-tailed)	0.18	0.011	0.39	0.66	

Owing to Table 4.18, correlation coefficient between the T (°c), pH, TDS (mg/l), DO (mg/l) and COD (mg/l) in the sampling wastewaters, showed that there is not any significant correlation between these parameters which may be related to the variability of petrochemical products and different processes in these companies.

### 4.3. Ecological Risk Assessment Based on Method of Lars Hakanson

According to method of Lars Hakanson (1980) the sedimentological-toxic factor and bioproduction index was determined then Toxic response factor ( $T_r$ ) based on this method were calculated.

BPI was calculated based on 10% of organic matter and the regression between the amount of nitrogen and percentage of organic matter. Thus, BPI was determined and its value was 4.22 (Fig.4.20).



**Fig.4.20.** Relationship between the organic content and N-content in Musa Bay sediments

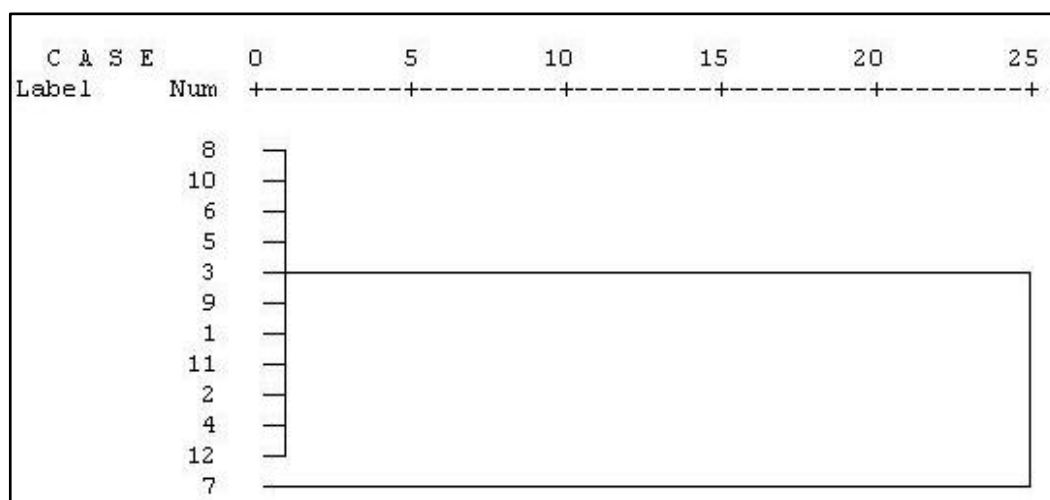
Sensitivity of aquatic organisms to toxic substances are strongly controlled by Bioproduction; it means that the toxicity of organic components such as PAHs and PCB increases with increasing Bioproduction (Hakanson, 1980). According to the previous study of Hakanson,  $S_t$  value (sedimentological-toxic) is equal 40;  $T_r$  is equal to  $40XBPI/5$  and  $RI = T_r \times Cf$ .

Thus contamination factor ( $C_f$ ) was calculated based on the guideline value (4200 ng/g) and the results of RI-value are shown in Table 4.21.

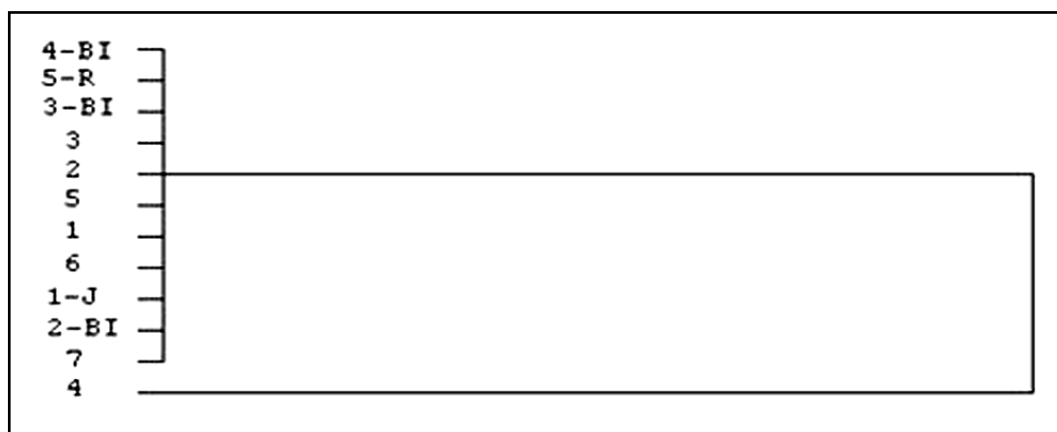
**Table 4.21.** Risk indices for investigated 12 stations in Musa Bay

No.	1	2	3	4	5	6	7	8	9	10	11	12
Station	1	1-J	2	2-BI	3	3-BI	4	4-BI	5	5-R	6	7
PAHs (ng/g)	646	454	1312	537	2713	1875	26659	2160	1410	2138	613	216
$C_f$	0.16	0.11	0.33	0.13	0.68	0.47	6.66	0.54	0.35	0.53	0.15	0.05
low $C_f < 1$	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓
moderate $1 \leq C_f < 3$												
considerable $3 \leq C_f < 6$												
very high $C_f \geq 6$							✓					
$RI = T_r * C_f$	5.47	3.84	11.10	4.55	22.95	15.86	225.54	18.28	11.93	18.09	5.19	1.83
Low ecological risk $RI < 50$	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓
Moderate ecological risk $50 \leq RI < 100$												
High ecological risk $100 \leq RI < 200$												
Very high ecological risk $RI \geq 200$							✓					

According to risk indices (RI-value) of 12 stations, contamination factor showed that this area is classified as low pollution according to contamination factor which was lower than 1, at almost all stations, except at station 4 (No.7). Thus the values of the risk index (RI) revealed that most of the stations except station 4 (No.7), are at low ecological risk.



**Fig.4.21.** Cluster analysis to classify stations based on ecological risk values in Musa bay



**Fig.4.22.** A dendrogram representation of a hierarchical cluster analysis of the PAHs in the Bay

Figure 4.21, represented the cluster analysis of stations based on ecological risk values and it showed that all the sampling stations can be categorized in a same group except station 4 (No.7) which is located near the Aromatic outlet of Bandar-e-Imam Khomeini petrochemical company. Also, the cluster analysis of PAHs in the sampling sediments confirmed that, this station (station 4) is categorized in the separate group from

other stations, as it shown in Figure 4.22 (Highest concentration of PAHs in the study area was observed at station 4).

Thus, according to the concentration of PAHs in the sediments and based on RI value this area can be classified as low ecological risk level; also, according to SQG method (PEL<sub>q</sub>) and the guideline of the Persian Gulf, this area can be classified as slightly polluted, based on the concentration of TPH.

#### **4.4. Identifying the Environmental Aspects and Determining the Environmental Impacts**

Environmental Impact Assessment was calculated based on the consequence of pollutant, probability, intensity and control index (based on 14001:2004), as follows.

Environmental impact = consequence x probability x intensity x control index.

According to the classification of TPH, the study area can classified as slightly polluted and risk index revealed that it is at low level risk category. Therefore, based on the TPH concentration in the sediments of the Musa Bay, the intensity is considered 2 in the study area (level 2); also, based on the ecological risk assessment the intensity is categorized in level 1 (Low ecological risk RI <50). While, probability is 5 for all of the sampling stations (because petrochemical companies discharge their effluents continuously) (level 5).

According to defined levels of pollutant consequence (in pervious section):

- I- Insignificant : (Unpolluted)  $1 < \text{TPH} \leq 5$ ;
- II- Minor: (Low)  $5 < \text{TPH} \leq 10$ ;

- III- Moderate: (Moderate)  $10 < \text{TPH} \leq 20$ ;
- IV- Major: (High)  $\text{TPH} \geq 20$ .

The classification of sampling effluents based on the concentration of TPH is as follows:

- I- BI-PC 2: level 4
- II- BI-PC 1 and R-PC: level 3
- III- ST-PC: level 2
- IV- Other sampling stations: level 1

The classification of sampling effluents based on the concentration of PAHs is level 1 for all of the sampling stations.

Also, the control index was defined in three levels and its classification for sampling stations is as follows:

- I- BI-PC 2, BI-PC 1 and R-PC: level 3
- II- ST-PC: level 2
- III- Other sampling stations: level 1

Finally, the Risk Priority Number (RPN) was calculated and the results are shown in Table 4.22.

**Table 4.22.** The Risk Priority Number based on TPH concentration in sampling effluents

No.	Station	RPN	RPN
1	AK-PC	10	Low environmental aspects
2	BI-PC 2	120	Important environmental aspects
3	BI-PC 1	90	moderate environmental aspects
4	ETP1	10	Low environmental aspects
5	ETP2	10	Low environmental aspects
6	EX-TANK	10	Low environmental aspects
7	F-PC	10	Low environmental aspects
8	FA-PC	10	Low environmental aspects
9	FR-PC	10	Low environmental aspects
10	GH-PC	10	Low environmental aspects
11	K-PC	10	Low environmental aspects
12	Kz-PC	10	Low environmental aspects
13	M-PC	10	Low environmental aspects
14	R-PC	90	moderate environmental aspects
15	SB-PC	10	Low environmental aspects
16	Treatment Plant (site 1)	10	Low environmental aspects
17	ST-PC	40	Low environmental aspects
18	STET	10	Low environmental aspects

1- **RPN  $\geq 192$ : is considered as significant environmental aspects** (should mitigate the risk and It requires immediate executive management attention, control action must be immediately implemented);

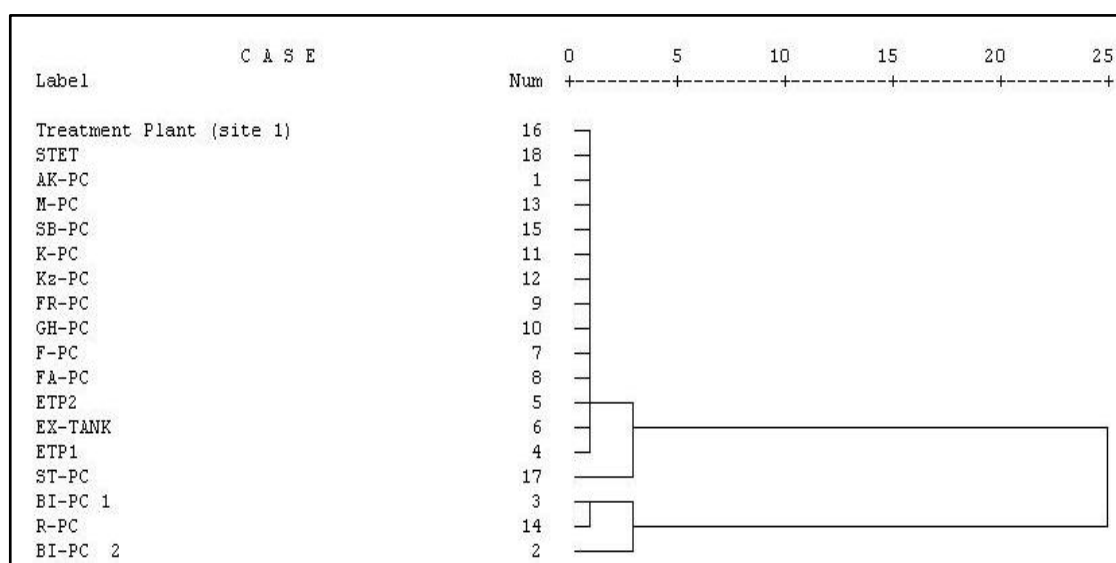
2-  **$100 < \text{RPN} < 191$ : is considered as an important environmental aspects**(should mitigate the risk and control action must be implemented);

3-  **$50 < \text{RPN} \leq 99$ : is considered as moderate environmental aspects** (should mitigate the risk in long term;

5-  **$0 < \text{RPN} \leq 49$ : is considered as low environmental aspects** (it does not need control actions but it should be monitored).

6-

The RPN showed that, station BI-PC2 is classified in a category of important environmental aspect, stations BI-PC1 and R-PC are categorized in moderate environmental aspects and other stations are considered as low environmental aspect.



**Fig.4.23.** Cluster analysis to classify stations based on RPN

The cluster analysis showed three significant groups. Thus it is demonstrated that the station No.2 (BI-PC2) is totally separated from other stations, while BI-PC1 and R-PC stations are clustered in the same group, differently from the other stations (Fig.4.23). Moreover, station No.17 (ST-PC) is classified in a distinct group from the rest of the stations which is related to the RPN of the station. Although calculation of RPN (Table4.22) showed that ST-PC is categorized under low environmental aspect but due to its high TPH concentration ( $>5$ ), the cluster analysis showed that it can be considered as a separate group than those other groups which are categorized in low environmental aspect.

In addition, according to the concentration of PAH in the sampling wastewaters (which was lower than the guideline value), the level of pollutant consequence is 1, the level of intensity is 1 and other factors are classified as same as the TPH. Thus, the RPN according to this pollutant was in the range of 0 and 59 (level 1); therefore it can be classified as low environmental aspect.



## **CHAPTER V: DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS**

### **5.1 Sediment Quality Assessment**

According to the sensitivity of this valuable aquatic ecosystem, in the present study, a combination of biological and physicochemical variables was monitored in Musa Bay, over multiple spatial and temporal scales because the distributions and effects of contaminants are influenced by water bodies, specific to the natural properties of the sediment, and the indigenous biological communities.

Results of the study demonstrated that fine-grained sediment was predominant at almost all stations (average 89.01% silt-clay); because there was not any significant difference for this parameter during the sampling time and in sampling stations, therefore, the bottom of the bed is muddy. Moreover, the results of this study were closed to the results of Dehghan-Madiseh (2007) which was showed that the concentration of TOM % fluctuated between 52.12- 96.18 % (Dehghan-Madiseh ,2007). Mooraki (2008), showed that the dominant composition of sediments in this area is fine materials (Mooraki,2008).Also the results of Manochehri (2009) showed that the bottom of the bed in this area is muddy (whit an average 89.07%) (Manochehri, 2009).

According to previous studies (Hedges & Keil, 1995; Meyers, et al., 1984), the concentration of organic matter in fine-grain sized sediments is greater than coarse-grain sized sediments. Thus the concentrations of TOM were monitored in the study area. The results of study showed a significant difference existed between the concentrations of organic matter in sampling station and four times sampling, which can be related to the

seasonal changes, tidal currents and other dominant water currents also other local changes that are the main causes of turbation (by effects on mobility) in this type of bottom sediments.

Also, previous studies in Musa Bay have shown that the percentage of TOM exceeded the guidelines (exceeding 1%) (EPA, 2002;Burone, Muniz, Pires-Vanin, Rodrigues , 2003 ) and the present study showed that the percentage of this parameter was in the range of previous studies of Manochehri (2009), which was about 12.93% in sediments of the Musa Bay (Manochehri, 2009). Moreover, results showed that the highest concentration of organic matter was observed at station 3-BI (No.6) which had the highest concentration of TPH. Therefore, this part of the Bay around the PETZONE is organic polluted (Dehghan-Madiseh, Nabavi, Ghofleh-Marammazi, Jahani, & Koochaknejad, 2012, Davies, 2009). The high total organic carbon and total organic matter concentrations in this Bay, might be attributed to the PETZONE and other surrounded industries.

Decomposition of the organic matter releases total organic carbon into the water which finally accumulates in the sediments (Davies, 2009).According to the high concentration of total organic carbon (with an average of 4.09%), it was used to calculate the benchmark of polycyclic aromatic hydrocarbon in the sediments of the study area.

At first, the concentration of PAHs in sampling sediments revealed that this parameter ranged from 216.57 (216.566931) to 26,659.07 (ng/g dry weight) with a mean value of 3394 .76 ng/g (3.40 µg/g). High concentration of PAHs was observed at station 4 (No.7) and the average concentration of PAHs in sampling stations of Musa Bay was lower than its concentration in the sediments of Musa Bay at Mahshahr oil export terminal ( 90 µg/g) and its concentration was very close to sediments of the Imam Khomeini port (0.19

- 3.52  $\mu\text{g/g}$ ), also concentration of PAHs was lower than in the other part of the RSA, near the BAPCO refinery in Bahrain (6.6  $\mu\text{g/g}$ ) (Tolosa, et al., 2005; Taatizadeh, 2009a).

In the next step, the following isomer ratios were used to identify potential sources of PAHs: Ant/ An+Phe, BaA/BaA + Chry, Flu/Flu + Pyr and IP/IP + Bghi. The Ant/Ant + Phe ratio showed that the main source of PAHs was combustion, while the Flu/Flu + Pyr ratio showed that at most stations, the main source of pollution was combustion of petroleum, except at stations 2-BI, 4 and 6, which received PAHs from different sources such as petrochemical industries especially Bandar-e-Imam Khomeini, shipping and other coastal industries. The BaA/BaA + Chry ratio showed that the main source of PAHs at all of the sampling stations was combustion and finally, the ratio of IP/IP+BP, at about half of the sampling stations showed that the main source of PAHs was petroleum origin input, while in the rest of them indicating that the input of PAHs were mainly from coal, wood and grass combustion.

In conclusion, Principal Components Analysis of PAHs and PAHs ratios in sampling sediment indicated that, in addition to petrogenic input as a major source of PAHs (because of the vast amount of oil and gas in the Persian Gulf), pyrolytic inputs are also a source for PAHs. In 2005, Ikenaka indicated that near-shore areas received both burnt material (pyrogenic) and oil products (petrogenic), whereas offshore stations were primarily influenced by burned material (Farrington, Goldberg, Risebrough, Martin, & Bowen, 1983; Ikenaka, Eun, Watanabe, Kumon, & Miyabara, 2005; Boonyatumanond, Wattayakorn, Togo, & Takada, 2006). The results of Mirza, et al., showed that the main sources of PAHs in the sediments of the Musa Bay (in five creeks) were mixed pyrolytic and petrogenic inputs (Mirza, et al., 2012).

In order to estimate the differences in bioavailability of PAHs in the sampling sediments, the sediment benchmark was calculated based on U.S. EPA PAH ESB approach (2010). The TOC concentration was used to calculate this benchmark and the result for Chronic Potency Ratio of 16PAHs showed that the chronic benchmark was not more than the guideline at all the stations (it is exceeded when the sum exceeds 1.0) except stations No. 6 (3-BI) and No. 7 (4), which had a highest concentration of TPH and PAHs respectively. Thus, the chronic benchmark at these stations indicates that they have the potential to cause a chronic effect on sediment-residence organisms such as crabs, clams and worms (US.EPA, 2010a).

Finally, the contamination factor was calculated based on the Hakanson method and it showed that the study area can be classified low polluted at all of the stations except station 4 (No.7) which was classified as very polluted (which is located near the Aromatic effluent outlet of Bandar-e-Imam Khomeini petrochemical company). Also the ecological risk based on this method showed that all of the stations are categorized in the Low ecological risk level except aforementioned station and the average concentration of PAHs was categorized under the Low ecological risk level. Several studies showed that high temperature (more than 20°C) and wind speed of more than 5.8 (Km/h) can increase the depletion rate of PAHs, thus the high temperature in this area (south of Iran), also the North wind which can cause water turbulence and self-purification in the Gulf area, could increase the depletion rate of PAHs (Guitart, García-Flor, Miquel, Fowler, & Albaigés, 2010; Montuori & Triassi, 2012).

In addition to PAHs, the concentrations of Total Petroleum Hydrocarbon (TPH) were evaluated in the sampling sediments. The results showed that although the

concentrations of TPH in this area is greater than the natural background value at all stations, its level increases to moderately polluted at stations 1,1-J,2,3-BI and 4\_BI and it reached the peak at station 3-BI. In conclusion, the levels of TPH concentration in the study area are relatively moderate (classified in slightly polluted level: 48.98  $\mu\text{g/g}$ ) compared to chronically oil-contaminated areas such as: The Gulf of Oman (0.05 - 779  $\mu\text{g/g}$ ) and also highly oil-contaminated coastline of BAPCO oil refinery in Bahrain (779  $\mu\text{g/g}$ ) (Tolosa, et al., 2005) , oil-contaminated coastline of Saudi Arabia after the Gulf war (11-6900  $\mu\text{g/g}$ ) (Readman, et al., 1996), near-shoreline marine sediments of the United Arab Emirates, in 1994 (0.4–212  $\mu\text{g/g}$ ), highly oil-impacted sediments of Hong Kong's Victoria Harbour (60-646  $\mu\text{g/g}$ ) (Hong, et al., 1995) and New York Bight (35–2900  $\mu\text{g/g}$ ) (Stephen de Mora , et al., 2010).

Moreover, the range of slightly toxic effects ( $0.1 < \text{PELq} < 0.5$ ) was detected for most of the stations which are located in the vicinity of the Bandar-e-Imam Khomeini and PETZONE effluent outlets. Also, the rest of the stations can be categorized in the range of non-toxic ( $\text{PELq} < 0.1$ ). In general, the average concentration of TPH and related PELq (49.98  $\mu\text{g/g}$  and 0.01, respectively) classified this area in the range of slightly toxic effects ( $0.1 < \text{PELq} < 0.5$ ).

## **5.2. Physical Parameters of Water**

The concentration of organic and inorganic pollutants in dissolved form is generally lower than particulate and colloidal forms, in aquatic ecosystems (Connell & Miller, 1984). The physicochemical parameters of an aquatic system control the adsorption, deposition and desorption rates of the pollutants in the water and sediment (Nduka & Orisakwe, 2011).

For example, the degradation rate of xenobiotics in marine or saline water is different than in fresh water (Tam, Guo, Yau, & Wong, 2002).

The pH is a primary indicator used to assess water quality and pollution in marine and coastal systems. In the study, fluctuation of this factor during 4 times sampling was between 7.82 to 8.80 and according to the suggested guideline, acceptable range for pH is 6.5–8.5 (WHO, 1993). Also the water temperature of the Bay was found to fluctuate between 15.80 °C to 35.60°C during 4 times sampling which was the normal range in this area and dissolved oxygen fluctuated between 4 mg/l and 6.80 mg/l. According to water quality score (WQS) for coastal waters based on (SCECAP, 2001) scores (Van Dolah, et al., 2004), the average concentration of dissolved oxygen in the study area was more than 4 (mg/l); therefore all values meet WQS and totally, all of the stations were over saturated with oxygen during the sampling period, so they were not impaired by pollution sources in the study area. Moreover, pH was greater than 7.4, thus according to WQS, this factor was not impaired too.

Generally, according to the results of the present study, it seemed that these factors (DO and pH) have no adverse effect on the distributions of TPH and PAHs, because these parameters remained within the acceptable standard range for marine and coastal water.

In addition, Two-Way ANOVA analysis showed significant difference ( $P < 0.05$ ) only in concentration of TDS (mg/l) in different stations and also during the sampling period, which can be related to seasonal variation and wastewater discharges. Fluctuation of this parameter depends on the season and the location with respect to the shoreline (Sabtan & Shehata, 2003).

### 5.3. Biological Response

Pearson and Rosenberg (1978) indicated that information on benthic macrofauna will help to provide an integrative measure for assessing and improving the ecological health of the ecosystem (Pearson & Rosenberg, 1978). Several parameters can constrain the structure of a benthic community such as hydrodynamic environment, food availability and anthropogenic stress (Rosenberg, 1976; Leonardsson, Blomqvist, & Rosenberg, 2009; Pacheco, Laudien, Thiel, Oliva, & Arntz, 2010). Several studies have been performed to determine the results of environmental deterioration by using benthic communities in the coastal areas of the world (Borja, Franco, & Pérez, 2000a; Gray, et al., 2002; Simboura & Zenetos, 2002).

In present study, nine groups of benthic organisms were identified at the 12 sampling stations during four sampling periods and Individual species of Tanaeidae 36% of the total abundance followed by Polychaeta (23%) and Bivalve (18%), Crustacea constituted 8%, were predominant in this area. Maximum abundance of Mollusca , Anthozoa and Gastropod (ind/m<sup>2</sup>) was observed at station No.12, Polychaet (ind/ m<sup>2</sup>) at station 6, Crustacea and Malacostraca at station 4, Barnachel at station No.11, Brachyryhyncha at station No.7 and Fish larva at stations No.2 and No.3. Large standard deviations in the total number of individuals indicated that temporal changes or inter-replicate differences varied strongly. In temporal scale, Crustacea were dominant while Brachyryhyncha and fish larva showed the lowest concentration in all sampling periods. Moreover, Benthic community was dominated by ecological group I and II (sensitive species) at stations No.1 and No.2 (I and I-J); thus, they are classified as slightly polluted. While stations, such as No.6 and No.7 (3-BI and 4- in the vicinity of BI-PC effluent outlets)

can be classified as heavily polluted and the benthic communities in these sites were dominated by ecological group V (opportunistic species). Also, ecological group III which are the tolerant species (to excess of organic matter enrichment) was observed at stations No.4 and No.5 (2-BI and 3); while ecological group IV (second order opportunist species) was not found in sampling stations

In total, the average value of AMBI was 2.66, so it can be categorized as slightly polluted. The pollution level of most of the stations varied between undisturbed and moderately polluted (except stations 3-BI and 4 which are heavily polluted and located in the vicinity of the BI-PC effluent outlets, also they have the highest concentration of TPH and PAH respectively). Also the results of Tabatabaie and Amiri (2011) confirmed that, at the stations around the sewage outlets in Musa Bay, water quality and DO decreased but the percentage of organic matter increased; moreover they had less macrobenthic species and higher Polychaetes (Tabatabaie & Amiri, 2011). Moreover, several studies showed that concentration of organic carbon and nitrogen increase in sediments close to discharge points and it has an adverse effect on macrobenthic communities. Therefore, as the concentration of organic matter increases, the abundance and biomass of macrobenthic communities especially Polychaeta increase (Devi and Ayyakkannu, 1989; Manochchri.2009). Therefore, as the benthic abundance and biomass decrease, fishery's rate decreases in Musa Bay too. Moreover, the negative correlation between abundance and biomass may be related to their small size or their low growth rate; this was confirmed by the previous researches such as (Manochchri 2009; kholfe ,2000).

According to AMBI, high condition was belonged to station No.2 and the bad condition was observed at station No.6 and No.7 (AMBI: 6, diversity and richness: 0)



which are located in the vicinity of BI-PC effluent outlets. The effect (one kind of the effects) of PAHs on the benthic community is that opportunistic species (ecological groups V and IV) with high abundances are replaced with other ecological groups (Rosenberg, 1976; Veiga, Rubal, & Besteiro, 2009); thus the benthic community of aforementioned stations was dominated by ecological group V (opportunistic species).

Also the results of benchmark values confirmed that these stations (No. 6 (3-BI) and No. 7 (4)) can have the potential to cause a chronic effect on sediment-residence organisms like crabs, clams and worms.

Other analysis that can help to assess benthic respond to contaminant is correlation analysis. In this research there was a significant negative correlation between Polychaeta, Tanaidacea, Brachyrehincha and Fish larva ( $r = -1$ ,  $r = -1$  and  $r = -0.999$  respectively). Thus the results indicated that as the abundances of Polychaeta increase, the abundance of aforementioned macrobenthic group decrease. Therefore stations NO. 6 and 7 (which were heavily polluted and dominated by ecological group V) had the lowest density of Tanaidacea, Brachyrehincha and Fish larva.

Also there was a negative correlation between the distributions of Crustacea, Tanaidacea and TPH ( $r = -0.845$ ,  $r = -1$  and  $r = -1$  respectively). Moreover, there was a significant negative correlation between Tanaidacea and PAHs ( $r = -1$ ). The results of correlations showed that, as the concentrations of TPH and PAHs increase, the abundance of Tanaidacea decrease, especially at stations No.6 and 7 (located in the vicinity of the BI-PC effluent outlets and had the highest concentrations of TPH and PAH respectively).

In conclusion the results showed that this area is still categorized as slightly polluted. Diaz and Rosenberg indicated that mass benthic mortality in heavily polluted areas is related to DO concentration when its concentration falls below than 2 (mg/l) (Diaz & Rosenberg, 1996); but the results of the study indicated that at all the sampling stations and during the sampling period, concentration of DO, was greater than the guideline value.

#### **5.4. Wastewater Quality Assessment**

Petrochemical industries have been verified as important emission sources and point source of a wide range of chemical substances, such as volatile compounds, heavy metals and POPs (persistent organic pollutants) (Nadal, et al., 2011). These impacts include not only the biological factors of the ecosystem but also water resource quality and human health (Esmaeli Sari, 2002).

According to the location of the Petrochemical Special Economic Zone (PETZONE), the hypothesis of the research , sensitivity of the Musa Bay; the quality of wastewater in the PETZONE wastewaters (in each active petrochemical company), was monitored based on the concentration of TPH and PAHs.

The results showed that the average concentration of TPH was lower than the guideline value at most of the stations, except the effluent outlets of the Razi and Imam Khomeini petrochemical (BI-PC) companies which are proximal to Musa Bay. Thus, they may have an adverse impact on the aquatic ecosystem of the Bay. Although Razi petrochemical company had high concentration of TPH in its effluent outlet during the sampling time; the concentration of TPH in the sediments which are located in the vicinity of the R-PC effluent outlet, was lower than those other stations. The present result may be

related to the high water depth at the site. But the concentration of TPH in sampling stations which are located in the vicinity of BI-PC effluent outlet (2, 2-BI, 3, 3-BI, 4 and 4-BI) was relatively moderate.

The high concentration of TPH at the aforementioned stations may be related to the nature of the petrochemical products and also it may be related to their old technologies which are established more than 30 years ago. Razi and Bandar-e-Imam Khomeini petrochemical companies have been established more than 30 years ago.

In addition to TPH, the concentration of PAHs in sampling stations was monitored and the average concentrations of  $\sum$ PAHs that effluents of the selected petrochemical company can be considered as unpolluted.

However, the results of Hosseini (2012) showed that the concentration of anthracene, pyrene and benzo(a)pyrene, in the water column of Jafari and Zangi creeks had the highest concentration of PAHs (Manochehri, 2009; Hosseini, et al., 2012); but, because these creeks are located inside the PETZONE area and connected to Musa Bay via connective canals they can be considered as effluent outlet. So, when effluents measured at the "end of pipe", it means that they were measured before release into the Bay, thus they are subsequently diluted in the Bay. Therefore, if the discharge concentrations of pollutant were more than the guidelines, it does not necessarily have a significant risk or it does not indicate that it may be contributing to a water quality standard exceeding in Musa Bay.

### 5.5. Other Physicochemical Parameter of Wastewater

Other important parameters that were measured in this study are, T (°C), pH, EC (µs/cm), TDS (mg/l), DO (mg/l) and COD (mg/l). The wastewaters had a pH ranging from 7 to 10.5; therefore most of the values meet the guidelines of "end of pipe" quality (for marine and coastal water), except for K-PC, GH-PC and BI-PC. The temperature of the wastewaters at all of the stations meet the guideline value except at station AK-PC (T°C <35). In addition to pH and temperature, the concentration of DO and TDS were lower than 3 (mg/l) and more than 1500 (mg/l) at most of the stations, respectively; and the high concentration of TDS was observed at BI-PC station (23645.9 mg/l).

Also, chemical oxygen demand (COD) was ranging from 57 to 697.1 (mg/l), and results showed that this parameter does not meet the "end of pipe" guideline quality at most of the stations except at stations , ET1, GH-PC, SB-PC and SITE. Moreover, the correlation coefficient between physicochemical parameters showed a significant negative correlation between DO and temperature and positive correlation between pH and TDS. Also there was a negative correlation between COD and DO (not significant).

Fluctuation of these parameters in the wastewater may be related to the products of each petrochemical company or other factors such as the cleaning processes including tanker cleaning and other related activities, and also sometimes can be related to emergency release. Therefore, the risk management program should be identified for these parameters and control actions should be implemented to reduce the environmental toxicity of excess amount of COD, pH and TDS.

## **5.6. Environmental Aspects and Determining the Environmental Impacts**

Environmental Impact assessment which is a study to determine, predict, evaluate and communicate information about the probable impacts of a recommended project on the surrounding environment to explain and list the mitigating measures should be performed before the project approval and implementation and should be continued during the project (Mustafa & Al-Bahar, 1991). So, it includes an extensive field which contains all activities that attempt to analyze and evaluate the effects of human stresses on natural and anthropogenic environments (Suter , et al., 1987). In general, environmental risk assessments is a process with several important objectives (LeVan, 1995) and it can be carried out on several levels.

In this study the effluent quality of selected petrochemical companies of the PETZONE was monitored approximately for every 2 months and assayed them for petroleum hydrocarbon pollution, and their environmental impacts and aspects was evaluated based on ISO 14001:2004.

The result of the equation is Risk Priority Number (RPN) and the calculation of RPN based on the TPH (the concentration in effluent outlets) showed that:

Station BI-PC2 is classified in a category of important environmental aspect, stations BI-PC1 and R-PC are categorized in moderate environmental aspects group and other stations are considered as low environmental aspect. As mentioned before, these companies have old technologies which are established more than 30 years ago.

Also, ST-PC was classified as low environmental aspect, but the cluster analysis showed that, it can be categorized in a separate group than those other low environmental

aspect group. The aforementioned difference is related to the higher concentration of TPH in the effluent outlet of ST-PC which was categorized in level 2 ( $5 < \text{TPH} \leq 10$ ), and it is probably related to the products of the company.

According to RPN, Bandar-e- Imam Khomeini petrochemical company (BI-PC) should mitigate the risk and control action must be implemented in this petrochemical company; also it requires executive management attention to reduce the risk and need to plan to reduce the risk of high petroleum hydrocarbon pollution to acceptable level (not immediately because it was not significant). But Razi petrochemical company had the lower level of the risk and should manage the risk and decrease it during the long term; because a comprehensive plan of risk reduction is directly related to its costs and management decision, also complete mineralization and treatment of the organic pollution is generally expensive (Xiong, et al., 2001).

According to results of the study, Shahid Tondgoyan petrochemical company can be considered as same as Razi petrochemical company and it is necessary for this company to mitigate the risk of petroleum hydrocarbon pollution during the long term and decrease it to acceptable level. In addition of these three petrochemical companies, other companies do not need any control action but they should be monitored during their activity.

In addition, according to the concentration of PAHs in the sediment and wastewater samples and also the RPN, it can be classified as low environmental aspects thus it does not need control actions but it should be monitored in the wastewaters of PETZONE.

## 5.7. Conclusion

The conclusions are described in the context of the objective and scope of the present research; thus they can be arranged as follows:

- 1- Fine-grained sediment was predominant at almost all stations (average 89.01% silt-clay); because there was not any significant difference for this parameter during the sampling time and in sampling stations, therefore, the bottom of the bed is muddy.
- 2- The percentage of TOM and TOC are exceeded the guideline values. Therefore, this part of the Bay around the PETZONE is organic polluted. Thus, the high total organic carbon and total organic matter concentrations in this Bay might be attributed to the PETZONE and other surrounded industries.
- 3- The results showed that although the concentration of TPH in this area is greater than the natural background value at all stations, its level increases to moderately polluted at stations 1,1-J,2,3-BI and 4\_BI and it reached the peak at station 3-BI. In conclusion, the levels of TPH concentration in the study area are relatively moderate (classified in slightly polluted level: 48.98 µg/g). Also the average concentration of TPH and related PELq (49.98 µg/g and 0.01, respectively) showed that this area can be classified in the range of slightly toxic effects ( $0.1 < \text{PELq} < 0.5$ ).
- 4- Average concentration of PAHs in the sampling sediments of the Musa Bay was lower than the guideline value. The source analysis of PAHs and PAHs ratios in sampling sediment indicated that, in addition to petrogenic input as a major

source of PAHs (because of the vast amount of oil and gas in the Persian Gulf), pyrolytic inputs are also a source for PAHs.

- 5- Chronic Potency Ratio of 16PAHs showed that the chronic benchmark was not more than the guideline at all the stations (it is exceeded when the sum exceeds 1.0) except stations 3-BI and 4, which had a highest concentration of TPH and PAHs respectively (they are located in the vicinity of Bandar-e-Imam Khomeini petrochemical company effluent outlets). Thus, the chronic benchmark at these stations indicates that they have the potential to cause a chronic effect on sediment-residence organisms such as crabs, clams and worms.
- 6- The contamination factor was calculated based on the Hakanson method and it showed that the study area can be classified low polluted at all of the stations except station 4 (No.7) which was classified as very polluted.
- 7- The average value of AMBI was 2.66, so it can be categorized as slightly polluted. The pollution level of most of the stations varied between undisturbed and moderately polluted (except stations 3-BI and 4 which are heavily polluted).
- 8- According to water quality score (WQS) for coastal waters based on (SCECAP, 2001) scores, the average concentration of dissolved oxygen in the study area was more than 4 (mg/l); therefore all values meet WQS and totally, all of the stations were over saturated with oxygen during the sampling period, so they were not impaired by pollution sources in the study area. Moreover, pH was greater than 7.4, thus according to WQS, this factor was not impaired too. Other physical parameters of water fluctuated between acceptable ranges in this area.
- 9- Owing to the results, the quality of the sediments in this area still can be categorized as slightly polluted and it might be related to the high concentration



of dissolved oxygen which was over saturated at almost all the sampling stations.

10- The results of the wastewater analysis showed that the average concentration of TPH was lower than the guideline value at most of the stations, except the effluent outlets of the Razi and Imam Khomeini petrochemical (BI-PC) companies which are proximal to Musa Bay. Thus, they may have an adverse impact on the aquatic ecosystem of the Bay. Because, Razi and Bandar-e-Imam Khomeini petrochemical companies have been established more than 30 years ago; thus, they have old technologies.

11- The concentration of PAHs in sampling stations was monitored and the average concentrations of PAHs that effluent of the selected petrochemical company can be considered as unpolluted.

12- Other important parameters of the effluents such as T (°c), pH, ( $\mu\text{s/cm}$ ), EC (mg/l), TDS (mg/l) and COD (mg/l), did not meet the guideline values at almost all stations, especially COD.

13- Environmental Impact Assessment was calculated based on the consequence of pollutant, probability, intensity and control index, as follows.

Environmental impact = consequence x probability x intensity x control index.

The result of the equation is Risk Priority Number (RPN) and the calculation of RPN based on the TPH, Station BI-PC2 is classified in a category of important environmental aspect, stations BI-PC1 and R-PC are categorized in moderate environmental aspects group and other stations are considered as low environmental aspect. Also, ST-PC was classified as low environmental aspect,

but the cluster analysis showed that, it can be categorized in a separate group than those other low environmental aspect group.

14- According to RPN, Bandar-e- Imam Khomeini petrochemical company (BI-PC) should mitigate the risk and control action must be implemented in this petrochemical company; also it requires executive management attention to reduce the risk and need to plan to reduce the risk of high petroleum hydrocarbon pollution to acceptable level (not immediately because it was not significant). But Razi petrochemical company had the lower level of the risk and should manage the risk and decrease it during the long term. Also, Shahid Tondgoyan petrochemical company should be considered as same as Razi petrochemical company.

15- In addition, according to the concentration of PAHs in the sediment and wastewater samples and also the RPN, it can be classified as low environmental aspects thus it does not need control actions but it should be monitored in the wastewaters of PETZONE.

16- In conclusion, the results of the wastewater quality based on TPH and PAHs showed that petrochemical special economic zone (PETZONE) is not the main source of oil pollution in this area. Also, despite the high concentration of anthropogenic contaminates and other non-point and point sources of pollution (such as shipping, Mahshahr oil export terminal and different industries), the results of the present study are unexpected in this semi-enclosed Bay with a slow rate of water exchange. The unusual results may be related to the deposition of finer sediments along the Iranian eastern side and northwest area, which is associated with the counter-clockwise circulation from the Indian Ocean,

deposition of eolian sediments, also the North wind which can cause water turbulence and self-purification in the Gulf area, probably the effects of tidal currents.

## **5.8. Recommendations**

According to the importance of Musa Bay, also importance of the PETZONE and its fundamental products, the present study recommended further investigations, as follows:

- 1- To study the concentrations of heavy metals in the wastewaters of the PETZONE petrochemical companies and also in the sediments of the Musa Bay;
- 2- To determine the preindustrial values in this area, also sediment redox potential (Eh) for better sediment quality assessment;
- 3- Conduct toxicity tests on biological communities on a laboratory scale to provide adequate data for human health risk assessments;
- 4- Monitor the water and sediments quality at the coastal area of the Bay, especially in Mahshahr oil export terminal which is approximately located in the northeast of the PETZONE and internal (unpublished) studies showed that it is heavily oil-polluted;
- 5- Monitor the concentrations of TPH, PAHs and heavy metals in the water column and sediments of Jafari and Zangi creeks (inside the PETZONE) as a separate research, also suggest useful and practical solutions to treat the water of these creeks before the entrance to the Musa Bay ;
- 6- The monthly production program of each petrochemical company should be determined to monitor petrochemical companies based on their production;
- 7- Monitor the effluent treatment plants (ETP1, ETP2, STET and treatment plant - site 1) separately and estimate their efficiency;

- 8- Modeling and simulation of final clarifiers in wastewater treatment plants of Razi and Bandar-e-Imam Khomeini petrochemical companies should be performed to dilute the wastewater concentration and decrease their adverse impacts;
- 9- Perform the process of sediment dredging around the PETZONE and coastal part of the Musa Bay annually;
- 10- The most important factor which was observed during the research is that, the effluent outlets of some petrochemical companies were not safe for sampling. Therefore, the workers and also the experts of the PETZONE environmental office (especially the expert who collects wastewater samples for the laboratory of PETZONE environmental office) need to be able to identify and deal with hazards associated with the space (workplace); also they have to understand the MSDS (Material Safety Data Sheet) of chemical products of each petrochemical company and follow the suggested recommendations of the personal protective equipment.

The significant risk is, they may fall into the wastewater canals during the sampling or during the work and it can cause several health problems. So it can be considered as serious threat, because some of effluent outlets of petrochemical companies do not have a safe area or safe railing and guards as it shown in Fig.5.1. Thus, assessing the health and safety risks should be performed to evaluate the risks and to suggest useful recommendations to decrease the significant risks in this area.



**Fig.5.1.** The effluent outlet of Bandar-e- Imam Khomeini and Shahid Tondgoyan petrochemical companies

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# APPENDIX



## Appendix I


### AI.1. Statistical description of Physical parameters in Musa Bay water

stations		T	PH	EC	TDS	DO	Salinity
1	Mean	22.8500	8.1150	5.7200E4	3.8896E4	4.7450	36.7000
	Maximum	27.60	8.18	5.80E4	3.94E4	5.38	36.90
	Minimum	18.10	8.05	5.64E4	3.84E4	4.11	36.50
	Std. Error of Mean	4.75000	.06500	8.00000E2	5.44000E2	.63500	.20000
	Std. Deviation	6.71751	.09192	1.13137E3	7.69332E2	.89803	.28284
2	Mean	22.4500	8.3400	5.4275E4	3.6907E4	4.9450	40.3500
	Maximum	27.00	8.80	5.50E4	3.74E4	5.89	40.90
	Minimum	17.90	7.88	5.35E4	3.64E4	4.00	39.80
	Std. Error of Mean	4.55000	.46000	7.75000E2	5.27000E2	.94500	.55000
	Std. Deviation	6.43467	.65054	1.09602E3	7.45291E2	1.33643	.77782
3	Mean	23.7500	8.2050	5.8900E4	4.0352E4	5.2150	39.2500
	Maximum	31.70	8.24	5.93E4	4.09E4	6.03	39.70
	Minimum	15.80	8.17	5.85E4	3.98E4	4.40	38.80
	Std. Error of Mean	7.95000	.03500	4.00000E2	5.72500E2	.81500	.45000
	Std. Deviation	1.12430E1	.04950	5.65685E2	8.09637E2	1.15258	.63640
4	Mean	23.4000	8.1650	5.9025E4	4.0137E4	5.1250	38.9500
	Maximum	28.90	8.21	5.92E4	4.02E4	5.68	39.10
	Minimum	17.90	8.12	5.89E4	4.01E4	4.57	38.80
	Std. Error of Mean	5.50000	.04500	1.25000E2	8.50000E1	.55500	.15000
	Std. Deviation	7.77817	.06364	1.76777E2	1.20208E2	.78489	.21213
5	Mean	23.7500	8.1850	6.0008E4	4.2005E4	4.9450	39.3500
	Maximum	29.00	8.20	6.00E4	4.20E4	5.34	39.60
	Minimum	18.50	8.17	6.00E4	4.20E4	4.55	39.10
	Std. Error of Mean	5.25000	.01500	2.50000	1.75000	.39500	.25000
	Std. Deviation	7.42462	.02121	3.53553	2.47487	.55861	.35355
6	Mean	25.0000	8.1600	5.6882E4	3.8981E4	5.2250	40.5500
	Maximum	31.20	8.19	5.80E4	4.00E4	6.02	42.30
	Minimum	18.80	8.13	5.58E4	3.80E4	4.43	38.80
	Std. Error of Mean	6.20000	.03000	1.07250E3	1.02980E3	.79500	1.75000
	Std. Deviation	8.76812	.04243	1.51674E3	1.45636E3	1.12430	2.47487

AI. (Continued) Statistical description of Physical parameters in Musa Bay water

stations		T	PH	EC	TDS	DO	Salinity
7	Mean	23.7500	7.8800	6.0625E4	4.2148E4	4.7000	39.3000
	Maximum	28.30	7.94	6.15E4	4.30E4	5.16	41.50
	Minimum	19.20	7.82	5.98E4	4.12E4	4.24	37.10
	Std. Error of Mean	4.55000	.06000	8.75000E2	9.02500E2	.46000	2.20000
	Std. Deviation	6.43467	.08485	1.23744E3	1.27633E3	.65054	3.11127
8	Mean	22.3000	7.8250	6.0900E4	4.2630E4	4.8750	41.7500
	Maximum	26.50	7.83	6.12E4	4.28E4	5.51	44.80
	Minimum	18.10	7.82	6.06E4	4.24E4	4.24	38.70
	Std. Error of Mean	4.20000	.00500	3.00000E2	2.10000E2	.63500	3.05000
	Std. Deviation	5.93970	.00707	4.24264E2	2.96985E2	.89803	4.31335
9	Mean	23.0000	8.1550	6.0425E4	4.2004E4	5.9400	40.1000
	Maximum	26.40	8.21	6.10E4	4.27E4	6.78	41.40
	Minimum	19.60	8.10	5.98E4	4.13E4	5.10	38.80
	Std. Error of Mean	3.40000	.05500	5.75000E2	6.96000E2	.84000	1.30000
	Std. Deviation	4.80833	.07778	8.13173E2	9.84293E2	1.18794	1.83848
10	Mean	23.0500	8.2050	5.8925E4	4.0069E4	5.3000	41.8500
	Maximum	27.00	8.30	5.90E4	4.01E4	5.50	44.90
	Minimum	19.10	8.11	5.89E4	4.01E4	5.10	38.80
	Std. Error of Mean	3.95000	.09500	2.50000E1	1.70000E1	.20000	3.05000
	Std. Deviation	5.58614	.13435	3.53553E1	2.40416E1	.28284	4.31335
11	Mean	22.2500	8.1300	5.8500E4	3.9780E4	4.8600	40.0000
	Maximum	25.00	8.20	5.85E4	3.98E4	5.10	43.30
	Minimum	19.50	8.06	5.85E4	3.98E4	4.62	36.70
	Std. Error of Mean	2.75000	.07000	.00000	.00000	.24000	3.30000
	Std. Deviation	3.88909	.09899	.00000	.00000	.33941	4.66690
12	Mean	23.1000	8.1800	6.3500E4	4.4450E4	6.7400	39.3500
	Maximum	28.10	8.28	6.35E4	4.44E4	6.80	39.50
	Minimum	18.10	8.08	6.35E4	4.44E4	6.68	39.20
	Std. Error of Mean	5.00000	.10000	.00000	.00000	.06000	.15000
	Std. Deviation	7.07107	.14142	.00000	.00000	.08485	.21213
Total	Mean	23.2208	8.1287	5.9097E4	4.0697E4	5.2179	39.7917
	Maximum	31.70	8.80	6.35E4	4.44E4	6.80	44.90
	Minimum	15.80	7.82	5.35E4	3.64E4	4.00	36.50
	Std. Error of Mean	1.05542	.04127	4.79667E2	4.20830E2	.17256	.46637
	Std. Deviation	5.17048	.20219	2.34988E3	2.06164E3	.84536	2.28472

## AI.2.Wastewater criteria at point of discharge to marine environment (Dubai)

Department of Planning & Development Ports, Customs & Free Zone Corporation Government of Dubai		 تراخيص Trakhees	دائرة التخطيط والتطوير مؤسسة الموانئ والجمارك والمنطقة الحرة حكومة دبي
Wastewater Criteria at Point of Discharge to Marine Environment / Harbor: Standards for Discharge of Wastewater to Harbor			
PARAMETERS <sup>(2)</sup>	SYMBOL	UNIT	MAXIMUM ALLOWABLE STANDARD <sup>(7)</sup>
Physical Properties			
Color	-	Color units	50
Total Suspended Solids	TSS	mg / l	50
Floating Particles	-	mg / m <sup>3</sup>	None
pH	-	pH units	6-9 <sup>(6)</sup>
Temperature <sup>(3)</sup>	T	°C	35 – maximum
Total Dissolved Solids	TDS	mg / l	1,500
Turbidity	-	NTU	75
Inorganic Chemical Properties			
Ammonia Total as (N)	NH <sub>4</sub> <sup>+</sup>	mg / l	2
Biochemical Oxygen Demand	BOD <sub>5</sub>	mg / l	50
Chemical Oxygen Demand	COD	-	100
Chlorine Residual <sup>(4)</sup> Total	Cl <sup>-</sup>	mg / l	1.0
Dissolved Oxygen <sup>(5)</sup>	DO	mg / l	> 3
Nitrate	NO <sub>3</sub> -N	mg / l	40
Sulfide	S <sup>-2</sup>	mg / l	0.1
Total Kjeldahl Nitrogen as (N)	TKN	mg / l	10
Total Phosphorous as (P)	PO <sub>4</sub> <sup>-3</sup>	mg / l	2
Trace Metals			
Aluminum	Al	mg / l	20
Antimony	Sb	mg / l	0.1
Arsenic	As	mg / l	0.05
Barium	Ba	mg / l	2
Beryllium	Be	mg / l	0.05
Cadmium	Cd	mg / l	0.05
Cyanide	CN	mg / l	0.05
Chromium, total	Cr	mg / l	0.2
Chromium, VI	Cr <sup>+6</sup>	mg / l	0.15
Cobalt	Co	mg / l	0.2
Copper	Cu	mg / l	0.5
Iron	Fe	mg / l	2
Environment, Health & Safety Division P.O. Box 17000, Dubai, United Arab Emirates 711 4 8811881 • Fax: +971 4 8818857 ehs.environment@trakhees.ae • Web Site: www.trakhees.ae			
إدارة البيئة والصحة والسلامة ص.ب. ١٧٠٠٠، دبي، الإمارات العربية المتحدة هاتف: ٨٨١١٨٨١ ٤ ٩٧١ • فاكس: ٨٨١٨٨٥٧ ٤ ٩٧١ البريد الإلكتروني: ehs.environment@trakhees.ae • الموقع الإلكتروني: www.trakhees.ae			

## AI.2. (Continued) Wastewater criteria at point of discharge to marine environment (Dubai)

Department of Planning & Development  
Ports, Customs & Free Zone Corporation  
Government of Dubai



دائرة التخطيط والتطوير  
مؤسسة الموانئ والجمارك والمنطقة الحرة  
حكومة دبي

Fluoride	F	mg / l	25
Lead	Pb	mg / l	0.1
Manganese	Mn	mg / l	0.2
Mercury	Hg	mg / l	0.001
Nickel	Ni	mg / l	0.1
Selenium	Se	mg / l	0.02
Silver	Ag	mg / l	0.005
Zinc	Zn	mg / l	0.5
Organic Chemical Properties			
Halogenated Hydrocarbons and Pesticides		mg/l	Nil
Hydrocarbons	HC	mg/l	15
Oil & Grease	O & G	mg/l	10
Phenols	-	mg/l	0.1
Solvent	-	mg/l	none
Total Organic Carbon	TOC	mg/l	75
Biological Properties			
Colon Group	TC	No. / 100 cm <sup>2</sup>	5,000
Egg Parasites	-	-	None
Fecal Coliform Bacteria	-	Cells / 100 mL	1,000
Total Coliform	-	MPN / 100 mL	1,000
Warm Parasites	-	-	None

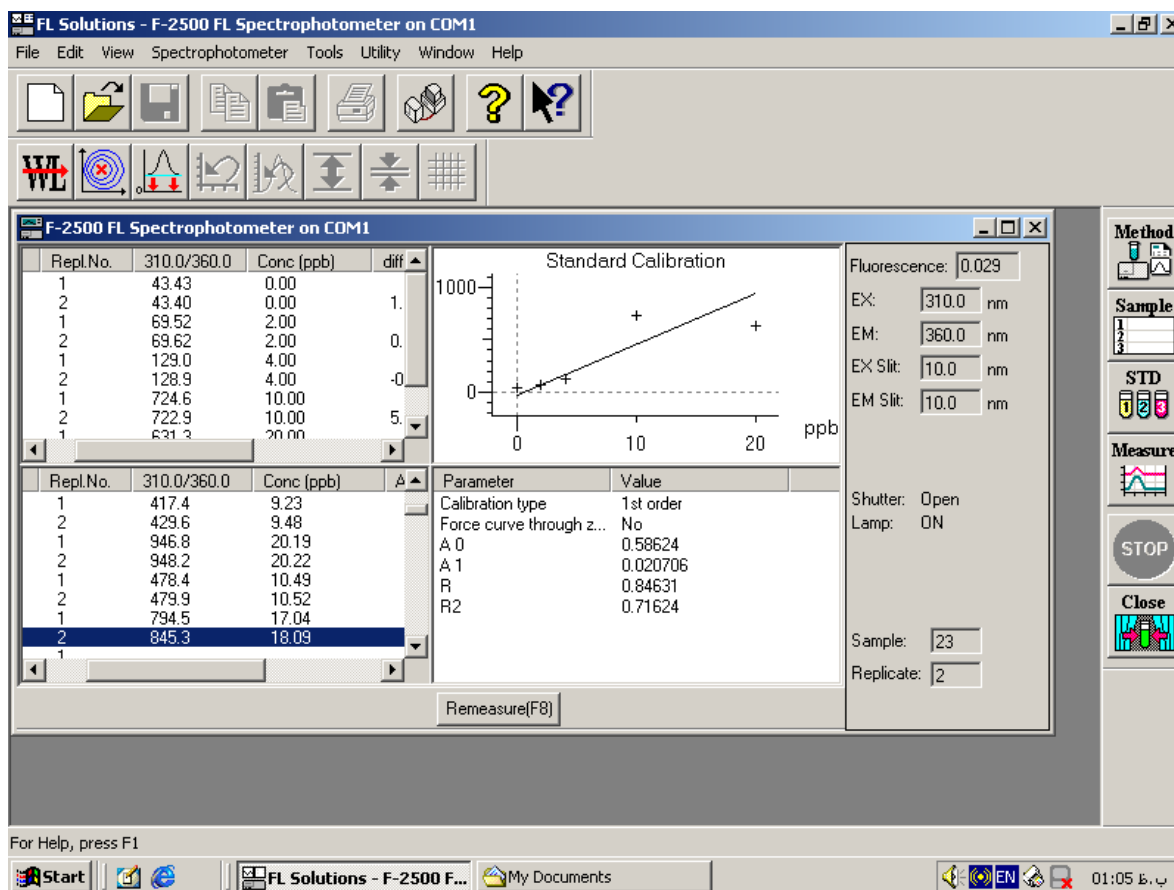
### Notes:

- 1) Any discharge to surface drainage must be authorized by JAFZA and shall only be permitted in exceptional circumstances.
- 2) For any parameters not identified, specific standards will be determined on a case-by-case basis.
- 3) The temperature increment standard for harbor discharge applies to treated wastewater/cooling water discharges.
- 4) Chlorine residual is after 30 minutes contact and is total residual chlorine
- 5) Dissolved oxygen requirement is a minimum concentration requirement
- 6) Inclusive range not to be exceeded.
- 7) With respect to Harbor Discharge Standard, FZ Companies should concentrate on full compliance of Harbour Discharge Standard.

Environment, Health & Safety Division  
P.O. Box 17000, Dubai, United Arab Emirates  
tel: +971 4 8811881 • fax: +971 4 8818857  
mail: ehs.environment@trakhees.ae • Web Site: www.trakhees.ae

إدارة البيئة والصحة والسلامة  
ص ب ١٧٠٠٠، دبي، الإمارات العربية المتحدة  
هاتف: ٨٨١١٨٨١ ٤ ٩٧١ • فاكس: ٨٨١٨٨٥٧ ٤ ٩٧١  
البريد الإلكتروني: ehs.environment@trakhees.ae • الموقع الإلكتروني: www.trakhees.ae

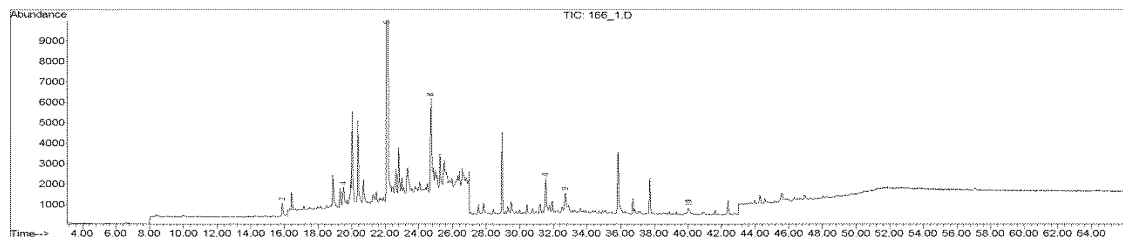
## Appendix II



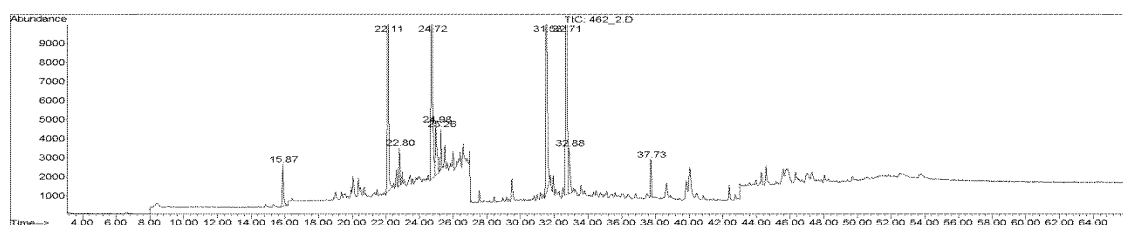
AII.1. Standard calibration graph of UV fluorescence,

(UVF- 2500- fixed excitation wavelength: 310 nm; the emission wavelength: 360 nm)

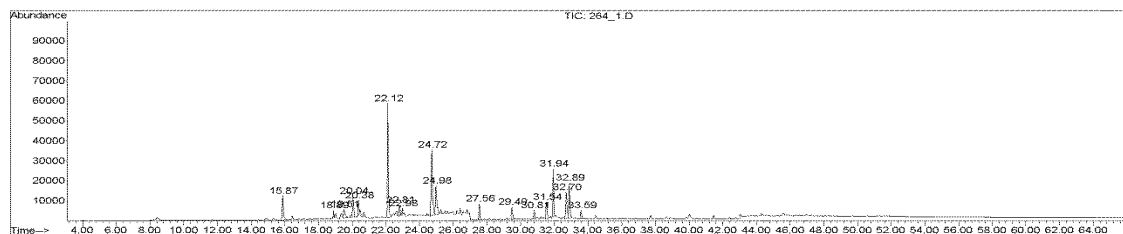
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 Acquired : 30 Jan 2011 15:29 using AcqMethod MOHEBBI3  
 Instrument : Instrumen  
 Sample Name: 54  
 Misc Info :  
 Vial Number: 54



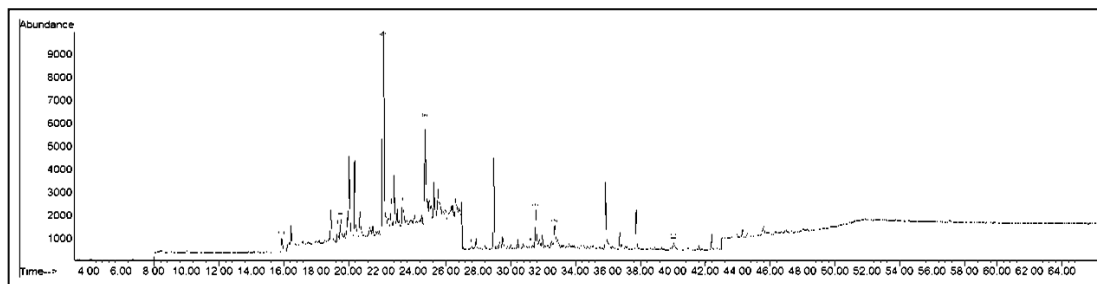
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 Acquired : 30 Jan 2011 21:55 using AcqMethod MOHEBBI3  
 Instrument : Instrumen  
 Sample Name: 59  
 Misc Info :  
 Vial Number: 59



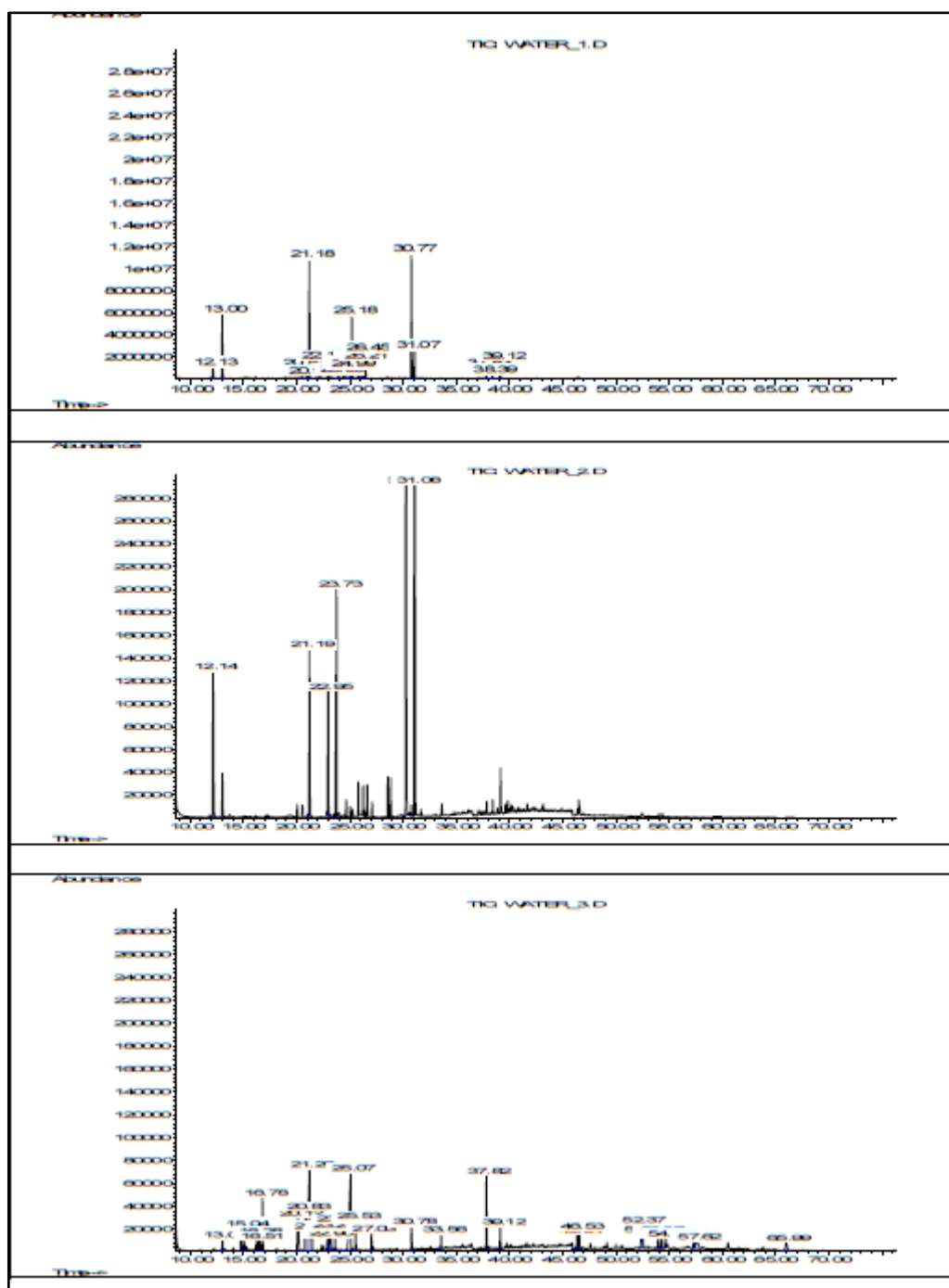
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 Operator :  
 Acquired : 30 Jan 2011 00:05 using AcqMethod MOHEBBI3  
 Instrument : Instrumen  
 Sample Name: 42  
 Misc Info :  
 Vial Number: 42



## A.II.2.Aromatic hydrocarbon profile of some sediment samples



## A.II.3.The chromatogram of Station BI-PC-Aromatic (sediment sample)



A.II.4.Aromatic hydrocarbon profile of some wastewater samples





A.II.5. station 2(No.3), BI-PC east pond outlet



A.II.6. station 3 (No.5), BI-PC southeastern outlet





A.II.7. station 4 (No.7), BI-PC Aromatic outlet



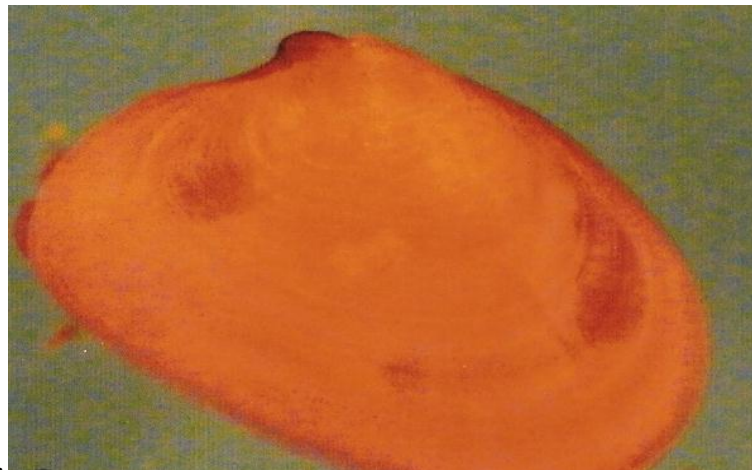
A.II.8. station 5 (No.9), in the vicinity of Razi petrochemical company effluent outlet



A.II.9.Southeast effluent outlet of BI-PC petrochemical company (inside the PETZONE)



A.II.10. Picture of Caprellidae in sample sediments



A.II.11. Picture of Telleridae in sample sediments



## Appendix III

explanation-of-pah-benchmark-calculations-20100622.doc  
6/23/2010 3:09:58 PM

### **Explanation of PAH benchmark calculations using EPA PAH ESB approach Originally developed by Dave Mount, ORD Duluth**

The effects of PAHs are cumulative (additive to be more precise) across all of the PAH compounds in petroleum. When you measure a single PAH, phenanthrene, for example, only a small percentage of the aggregate effect of the petroleum-contaminated mixture is measured.

The "potency divisors" used in the calculation represent the amount of an individual chemical (ie phenanthrene), by itself, that can cause an adverse effect. So, if there was a spill that was nothing but pure phenanthrene, the "potency divisor" for phenanthrene would be the same as the effect level for phenanthrene alone, and one would just compare the two numbers.

#### **PAH Benchmark Calculation for Water Samples**

In the case of oil, phenanthrene is just one chemical that contributes to the overall potency of the petroleum mixture. To determine the overall effect of the petroleum in water, one must combine the contributions of all the individual chemicals in the petroleum mixture. The effect of the mixture can be calculated by simply adding together the fractional contributions of all of the components of the mixture. So to estimate the total effect of the mixture of PAHs in an oil sample, first you divide each of the individual compounds by the potency divisor (explained above), then the ratios are added together to calculate the combined toxicity. (See example calculation on page 5)

#### **PAH Benchmark Calculation for Sediment Samples**

To determine PAHs in sediment, it is important to factor in the amount of organic carbon in the sediment. When organic carbon is present in sediment, PAHs bind to the organic carbon, making the PAHs less available to aquatic life, thus lessening their toxicity. For example, both sediments A and B have measured phenanthrene concentrations of 10,000 ug/kg dry weight. Sediment A has an organic carbon concentration of 1% and Sediment B has an organic carbon concentration of 2%. Sediment B is considered half as toxic as Sediment A, because Sediment B can bind twice the amount of phenanthrene than Sediment A.

In order to account for the differences in bioavailability, the dry weight-based PAH concentrations measured in sediment are divided by the organic carbon concentration. From the example above, the phenanthrene concentration of 10,000 ug/kg dry weight in Sediment A is divided by 0.01 (1%) kg organic carbon to equal 1,000,000 ug phenanthrene/kg organic carbon. The phenanthrene concentration of 10,000 ug/kg dry weight in Sediment B is divided by 0.02 (2%) kg organic carbon to equal 500,000 ug phenanthrene/kg organic carbon. Sediment B has a lower organic carbon-normalized phenanthrene concentration, reflective of the lower bioavailability of phenanthrene in Sediment B.

A more complex sediment example is as follows:

A sediment sample contains

9.23 ug/kg dry weight pyrene  
10.00 ug/kg dry weight naphthalene  
10.00 ug/kg dry weight phenanthrene  
20.00 ug/kg dry weight fluoranthene  
3.5% or 0.035 organic carbon concentration

1. Normalize the PAH concentrations by dividing by the fraction organic carbon:

$(9.23 \text{ ug pyrene/kg dwt}) / (0.035 \text{ kg organic carbon/kg dwt}) = 263.7 \text{ ug pyrene/kg organic carbon}$   
 $(10.00 \text{ ug naphthalene/kg dwt}) / (0.0035 \text{ kg organic carbon/kg dwt}) = 285.7 \text{ ug naphthalene/kg organic carbon}$   
 $(10.00 \text{ ug phenanthrene/kg dwt}) / (0.0035 \text{ kg organic carbon/kg dwt}) = 285.7 \text{ ug phenanthrene/kg organic carbon}$   
 $(20.00 \text{ ug fluoranthene/kg dwt}) / (0.0035 \text{ kg organic carbon/kg dwt}) = 571.4 \text{ ug fluoranthene/kg organic carbon}$

2. Divide these organic carbon-normalized values by their "potency divisors" from the sediment benchmark table. The chronic "potency divisors" are:

pyrene = 697,000 ug/kg organic carbon  
naphthalene = 385,000 ug/kg organic carbon  
phenanthrene = 596,000 ug/kg organic carbon  
fluoranthene = 707,000 ug/kg organic carbon

These calculations yield

$(263.7 \text{ ug pyrene/kg organic carbon}) / (697,000 \text{ ug/kg organic carbon}) = 0.000378$   
 $(285.7 \text{ ug naphthalene/kg organic carbon}) / (385,000 \text{ ug/kg organic carbon}) = 0.000742$   
 $(285.7 \text{ ug phenanthrene/kg organic carbon}) / (596,000 \text{ ug/kg organic carbon}) = 0.000479$   
 $(571.4 \text{ ug fluoranthene/kg organic carbon}) / (707,000 \text{ ug/kg organic carbon}) = 0.000808$

These numbers are basically the fraction of a chronically toxic concentration represented by that single compound. So the concentration of pyrene is basically 0.000378 or 0.0378% of the amount of pyrene alone that would be required to cause toxicity.

3. Add the individual fractional contributions of each PAH compound together, since the toxicity of the compounds are additive:

$0.000378 \text{ pyrene} + 0.000742 \text{ naphthalene} + 0.000479 \text{ phenanthrene} + 0.000808 \text{ fluoranthene} =$

0.002407

The chronic benchmark is exceeded when the sum exceeds 1.0. In this example, the PAH concentration in the sample is well below a toxic concentrations.

The previous example is based on four PAH compounds out of 100's that are in oil. To determine the combined potency or toxicity, the calculation procedure must be completed for all of the PAHs present in the sample. The potency of oil lies outside the dozen or so PAHs often measured.

In addition to PAHs, the BTEX compounds will also add to the overall potency of petroleum. While EPA is measuring for these chemicals in oil, it is unlikely that BTEX will remain in the samples by the time Deepwater Horizon petroleum reaches shore. This is because these chemicals are volatile, and quickly evaporate into the air when oil reaches the surface of the ocean. If there was BTEX chemicals left, it would add to the potency of the PAHs. The calculations are done exactly the same, but you just include the potency ratios (concentration/potency divisor) for those compounds in the sum also.

#### Consideration of samples without alkylated PAHs

When evaluating a sample in which the alkylated PAHs were not measured, you must compensate for their contribution by using "alkylation multipliers". These multipliers account for the unmeasured alkyl compounds that are missed. The multipliers were created based the reported analysis of the Dauphin Island tar ball from the current spill, but were then also checked against oil composition data from other sources, including the Exxon Valdez oil.

For example, the multiplier for naphthalene is 120. That is because this analysis shows that the concentrations of alkylated naphthalenes exceeds the concentration of naphthalene itself. The total potency of all the naphthalene compounds (alkylated and not), were calculated and compared to the ratio of the potency of naphthalene alone. This ratio was 118 (which was rounded to 120). In this case, 99.2% of the real potency of all naphthalene compounds is caused by alkyl-substituted naphthalenes rather than naphthalene itself. To account for this, the alkylation multipliers increase the concentration of naphthalene to account for the unmeasured material.

So, in the example calculation above, we had the organic carbon normalized concentrations calculated as:

$$(9.23 \text{ ug pyrene/kg dwt}) / (0.035 \text{ kg organic carbon/kg dwt}) = 263.7 \text{ ug pyrene/kg organic carbon}$$

$$(10.00 \text{ ug naphthalene/kg dwt}) / (0.0035 \text{ kg organic carbon/kg dwt}) = 285.7 \text{ ug naphthalene/kg organic carbon}$$



$(10.00 \text{ ug phenanthrene/kg dwt}) / (0.0035 \text{ kg organic carbon/kg dwt}) = 285.7 \text{ ug phenanthrene/kg organic carbon}$

$(20.00 \text{ ug fluoranthene/kg dwt}) / (0.0035 \text{ kg organic carbon/kg dwt}) = 571.4 \text{ ug fluoranthene/kg organic carbon}$

and alkylation multipliers apply to three of the four compounds as follows:

pyrene = 2.1

naphthalene = 120

phenanthrene = 6.8

So the concentrations adjusted for alkylation would be:

$263.7 \text{ ug pyrene/kg organic carbon} * 2.1 = 553.8 \text{ ug pyrene/kg organic carbon}$

$285.7 \text{ ug naphthalene/kg organic carbon} * 120 = 34280 \text{ ug naphthalene/kg organic carbon}$

$285.7 \text{ ug phenanthrene/kg organic carbon} * 6.8 = 1943 \text{ ug phenanthrene/kg organic carbon}$

$571.4 \text{ ug fluoranthene/kg organic carbon} * 1 \text{ (no multiplier)} = 571.4 \text{ ug fluoranthene/kg organic carbon}$

Completing the calculation as above, these values are divided by the potency divisors:

$(553.8 \text{ ug pyrene/kg organic carbon}) / (697,000 \text{ ug/kg organic carbon}) = 0.000795$

$(34280 \text{ ug naphthalene/kg organic carbon}) / (385,000 \text{ ug/kg organic carbon}) = 0.0890$

$(1943 \text{ ug phenanthrene/kg organic carbon}) / (596,000 \text{ ug/kg organic carbon}) = 0.00326$

$(571.4 \text{ ug fluoranthene/kg organic carbon}) / (707,000 \text{ ug/kg organic carbon}) = 0.000808$

The sum of these is 0.094, which means it still meets the guideline (because the sum is less than 1), but it indicates a much higher level of contamination than in the original calculation. See example calculation on page 6.

## Example PAH Sediment Benchmark Calculation

Sediment TOC (mg/kg dwt) 35000

CHEMICAL	Column A Measured Concentrations (ug/kg dwt)	Column B Organic Carbon Normalized Concentrations (ug/kg OC)	Column C Alkylation Multiplier	Column D Alkyl-Adjusted Concentrations (ug/kg OC)	Column E Acute Potency Divisor (ug/kg Organic Carbon)	Column F Chronic Potency Divisor (ug/kg Organic Carbon)	Column G Acute Potency Ratio	Column H Chronic Potency Ratio
Benzene	0	0	1	0	3,390,000	660,000	0.00000	0.00000
Cyclohexane	0	0	1	0	4,000,000	786,000	0.00000	0.00000
Ethylbenzene	0	0	1	0	4,930,000	970,000	0.00000	0.00000
Isopropylbenzene	0	0	1	0	5,750,000	1,130,000	0.00000	0.00000
m-Xylene	0	0	1	0	4,980,000	980,000	0.00000	0.00000
p-Xylene	0	0	1	0	4,980,000	980,000	0.00000	0.00000
o-Xylene	0	0	1	0	4,980,000	980,000	0.00000	0.00000
Methylcyclohexane	0	0	1	0	4,980,000	976,000	0.00000	0.00000
Toluene	0	0	1	0	4,120,000	810,000	0.00000	0.00000
<b>Naphthalene</b>	10	286	120	34286	1,600,000	385,000	0.02143	0.08905
Acenaphthylene	0	0	1	0	1,880,000	452,000	0.00000	0.00000
Acenaphthene	0	0	1	0	2,040,000	491,000	0.00000	0.00000
Fluorene	0	0	14	0	2,240,000	538,000	0.00000	0.00000
<b>Phenanthrene</b>	10	286	6.8	1943	2,480,000	596,000	0.00078	0.00326
Anthracene	0	0	1	0	2,470,000	594,000	0.00000	0.00000
<b>Fluoranthene</b>	20	571	1	571	2,940,000	707,000	0.00019	0.00081
<b>Pyrene</b>	9.23	264	2.1	554	2,900,000	697,000	0.00019	0.00079
Benz(a)anthracene	0	0	1	0	3,500,000	841,000	0.00000	0.00000
Chrysene	0	0	5	0	3,510,000	844,000	0.00000	0.00000
Perylene	0	0	1	0	4,020,000	967,000	0.00000	0.00000
Benzofluoranthene	0	0	1	0	4,070,000	979,000	0.00000	0.00000
Benzok)fluoranthene	0	0	1	0	4,080,000	981,000	0.00000	0.00000
Benzofluorene	0	0	1	0	4,020,000	967,000	0.00000	0.00000
Benzol(a)pyrene	0	0	1	0	4,020,000	985,000	0.00000	0.00000
Indeno(1,2,3-cd)pyrene	0	0	1	0	4,620,000	1,110,000	0.00000	0.00000
Dibenz(a,h)anthracene	0	0	1	0	4,660,000	1,120,000	0.00000	0.00000
Benzol(g,h)perylene	0	0	1	0	4,540,000	1,090,000	0.00000	0.00000

Legend	Reported Concentrations	Reported Concentrations
White = measured value from sample	Reported Concentrations	Reported Concentrations
Turquoise = given values	Reported Concentrations	Reported Concentrations
Tan = calculated values	Reported Concentrations	Reported Concentrations
	<b>TOTAL</b>	<b>0.023 0.064</b>
	DO NOT	DO NOT
	DO NOT	DO NOT

exceed acute benchmark because total value is less than 1  
exceed chronic benchmark because value is less than 1

STEP 1: Divide Column A by TOC, then Multiply by 1,000,000. The result is Column B.

STEP 2: Multiply Column B by Column C. The result is Column D.

STEP 3a: Divide Column D by Column E. The result is Column G.

STEP 3b: Divide Column D by Column F. The result is Column H.

STEP 4a: Sum Column G for Acute Benchmark Value.

STEP 4b: Sum Column H for Chronic Benchmark Value.